

FINAL

**Treatability Study in Support of
Intrinsic Remediation for Site OT 24
Volume I of II**



**MacDill Air Force Base
Tampa, Florida**

Prepared For

**Air Force Center for Environmental Excellence
Technology Transfer Division
Brooks Air Force Base
San Antonio, Texas**

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FINAL
TREATABILITY STUDY IN SUPPORT OF
INTRINSIC REMEDIATION FOR
SITE 0T 24

at

MACDILL AIR FORCE BASE
TAMPA, FLORIDA

VOLUME I of II

January 1997

Prepared for:

AIR FORCE CENTER FOR ENVIRONMENTAL EXCELLENCE
TECHNOLOGY TRANSFER DIVISION
BROOKS AIR FORCE BASE
SAN ANTONIO, TEXAS

AND

6 CES/CEVR
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TABLE OF CONTENTS

	<u>Page</u>
EXECUTIVE SUMMARY	ES-1
SECTION 1 - INTRODUCTION	1-1
1.1 Scope and Objectives	1-1
1.2 Facility and Site Background	1-3
SECTION 2 - SITE CHARACTERIZATION ACTIVITIES.....	2-1
2.1 Geoprobe®, Soil and Sediment Sampling and Monitoring Point Installation	2-2
2.1.1 Groundwater Monitoring Point Locations and Completion Intervals	2-2
2.1.2 Groundwater Monitoring Point Placement and Soil Sampling Procedures.....	2-2
2.1.2.1 Geoprobe® Clearance Activities.....	2-2
2.1.2.2 Equipment Decontamination Procedures.....	2-6
2.1.2.3 Borehole Advancement and Soil/Sediment Sampling	2-6
2.1.3 Monitoring Point Installation	2-9
2.1.3.1 Monitoring Point Materials Decontamination.....	2-9
2.1.3.2 Monitoring Point Casing and Screen.....	2-9
2.1.3.3 Sand Filter Pack.....	2-10
2.1.3.4 Annular Sealant	2-10
2.1.3.5 Flush-Mount Protective Cover	2-10
2.1.4 Monitoring Point Development.....	2-11
2.2 Groundwater Sampling	2-11
2.2.1 Groundwater Sampling Locations.....	2-11
2.2.2 Preparation and Equipment Cleaning.....	2-11
2.2.3 Groundwater Sampling Procedures	2-12
2.2.3.1 Preparation of Location	2-12
2.2.3.2 Water Level and Total Depth Measurements	2-12
2.2.3.3 Monitoring Well/Point Purging	2-13
2.2.3.4 Sample Collection.....	2-13
2.2.4 Onsite Chemical Parameter Measurement	2-13
2.2.4.1 Dissolved Oxygen Measurements.....	2-13
2.2.4.2 Electrical Conductivity, pH, Redox Potential, and Temperature Measurements	2-14
2.2.4.3 Hach® and CHEMetrics® Field Chemistry Measurements ...	2-14
2.2.5 Sample Handling	2-14
2.2.5.1 Sample Containers, Preservation, and Labels.....	2-14
2.2.5.2 Sample Shipment.....	2-15

TABLE OF CONTENTS (Continued)

	<u>Page</u>
2.3 Aquifer Testing	2-15
2.4 Surveying	2-15
SECTION 3 - PHYSICAL CHARACTERISTICS OF THE STUDY AREA.....	3-1
3.1 Vegetation Characteristics, Ground Surface Topography and Surface Water Hydrology	3-1
3.2 Climate	3-2
3.3 Manmade Features	3-2
3.4 Regional Geology and Hydrogeology	3-2
3.5 Site Geology and Hydrogeology	3-3
3.6 Groundwater Use.....	3-12
SECTION 4 - NATURE AND EXTENT OF CONTAMINATION AND SOIL AND GROUNDWATER GEOCHEMISTRY.....	4-1
4.1 Sources Of Contamination	4-1
4.1.1 Source of Fuel Releases	4-1
4.1.2 Extent of Free Product	4-1
4.2 Soil Chemistry	4-3
4.2.1 Soil and Sediment Headspace Screening	4-3
4.2.2 Magnitude and Extent of BTEX and Total Petroleum Hydrocarbons in Soil and Sediment	4-3
4.2.3 Total Organic Carbon.....	4-8
4.3 Groundwater Chemistry	4-8
4.3.1 Dissolved Hydrocarbon Contamination	4-10
4.3.1.1 Dissolved BTEX Contamination	4-10
4.3.1.2 Dissolved TPH Contamination	4-15
4.3.1.3 Chlorinated Volatile Organic Compounds.....	4-15
4.3.2 Inorganic Chemistry and Geochemical Indicators of BTEX Biodegradation	4-17
4.3.2.1 Dissolved Oxygen.....	4-20
4.3.2.2 Nitrate/Nitrite.....	4-24
4.3.2.3 Ferrous Iron.....	4-24
4.3.2.4 Sulfate	4-26
4.3.2.5 Methane	4-28
4.3.2.6 Reduction/Oxidation Potential	4-30
4.3.2.7 Alkalinity.....	4-30
4.3.2.8 pH.....	4-33
4.3.2.9 Temperature	4-33
4.3.2.10 Expressed Assimilative Capacity	4-33

TABLE OF CONTENTS (Continued)

	<u>Page</u>
4.3.3 Processes of Intrinsic Remediation for Chlorinated Solvents	4-35
4.3.3.1 Electron Acceptor Reactions (Reductive Dehalogenation) ...	4-35
4.3.3.2 Electron Donor Reactions.....	4-37
4.3.3.3 Cometabolism	4-37
4.3.3.4 Biodegradation of Chlorinated Solvents at Site OT 24	4-39
SECTION 5 - GROUNDWATER MODEL	5-1
5.1 General Overview and Model Description.....	5-1
5.2 Conceptual Model Design and Assumptions	5-2
5.3 Initial Model Setup.....	5-2
5.3.1 Grid Design and Boundary Conditions	5-3
5.3.2 Groundwater Elevation and Gradient.....	5-5
5.3.3 BTEX Concentrations.....	5-6
5.3.4 Dissolved Oxygen	5-7
5.3.5 Anaerobic Degradation Rates.....	5-8
5.4 Model Calibration.....	5-9
5.4.1 Water Table Calibration	5-11
5.4.2 BTEX Plume Calibration.....	5-16
5.4.2.1 Dispersivity	5-19
5.4.2.2 Anaerobic Decay Rate Constant	5-20
5.4.2.3 Coefficient of Retardation	5-20
5.4.2.4 Source Injection Concentration	5-20
5.5 Sensitivity Analysis	5-22
5.5.1 Sensitivity to Variations in Transmissivity.....	5-28
5.5.2 Sensitivity to Variations in the Coefficient of Retardation	5-28
5.5.3 Sensitivity to Variations in the Anaerobic Decay Rate Constant	5-29
5.5.4 Sensitivity to Variations in Dispersivity.....	5-29
5.5.5 Sensitivity to Variations in Injected BTEX Concentrations	5-31
5.5.6 Summary of Sensitivity Analysis Results	5-31
5.6 Model Results.....	5-31
5.6.1 Diminishing BTEX Source (Model OT 24A)	5-32
5.6.2 Engineered Source Reduction (Model OT 24B)	5-33
5.6.3 Engineered Source Reduction and Groundwater Extraction (Model OT 24C).....	5-38
5.7 Conclusions and Discussion	5-40
SECTION 6 - COMPARATIVE ANALYSIS OF REMEDIAL ALTERNATIVES	6-1
6.1 Remedial Alternative Evaluation Criteria.....	6-1
6.1.1 Long-Term Effectiveness and Permanence	6-1

TABLE OF CONTENTS (Continued)

	<u>Page</u>
6.1.2 Implementability	6-2
6.1.3 Cost	6-2
6.2 Factors Influencing Alternatives Development	6-2
6.2.1 Program Objectives	6-2
6.2.2 Contaminant Properties	6-3
6.2.3 Site-Specific Conditions	6-5
6.2.3.1 Groundwater and Soil Characteristics	6-5
6.2.3.2 Potential Exposure Pathways	6-6
6.2.3.3 Remediation Goals for Shallow Groundwater	6-8
6.2.4 Summary of Remedial Option Screening	6-10
6.3 Brief Description of Remedial Alternatives	6-10
6.3.1 Alternative 1--Intrinsic Remediation and Institutional Controls with Long-Term Groundwater Monitoring	6-10
6.3.2 Alternative 2--Bioventing/Biosparging in Source Area, Intrinsic Remediation, and Institutional Controls with Long-Term Groundwater Monitoring	6-16
6.3.3 Alternative 3--Groundwater Extraction, Bioventing/Biosparging in Source Area, Intrinsic Remediation, and Institutional Controls with Long-Term Groundwater Monitoring	6-17
6.4 Evaluation of Alternatives	6-17
6.4.1 Alternative 1--Intrinsic Remediation and Institutional Controls with Long-Term Groundwater Monitoring.	6-18
6.4.1.1 Effectiveness	6-18
6.4.1.2 Implementability	6-18
6.4.1.3 Cost	6-19
6.4.2 Alternative 2 - Bioventing/Biosparging in Source Area, Intrinsic Remediation, and Institutional Controls with Long-Term Groundwater Monitoring	6-21
6.4.2.1 Effectiveness	6-21
6.4.2.2 Implementability	6-21
6.4.2.3 Cost	6-22
6.4.3 Alternative 3--Groundwater Extraction, Bioventing/Biosparging in Source Area, Intrinsic Remediation, and Institutional Controls with Long-Term Groundwater Monitoring	6-22
6.4.3.1 Effectiveness	6-22
6.4.3.2 Implementability	6-24
6.4.3.3 Cost	6-24
6.5 Recommended Remedial Approach	6-26

TABLE OF CONTENTS (Continued)

	<u>Page</u>
SECTION 7 - LONG-TERM MONITORING PLAN	7-1
7.1 Overview	7-1
7.2 Monitoring Networks	7-3
7.2.1 Long-Term Monitoring Wells	7-3
7.2.2 Point-of-Compliance Wells	7-4
7.3 Groundwater Sampling	7-4
7.3.1 Analytical Protocol	7-5
7.3.2 Sampling Frequency	7-5
SECTION 8 - CONCLUSIONS AND RECOMMENDATIONS	8-1
SECTION 9 - REFERENCES	9-1

APPENDICES

- Appendix A - Information from CH2M Hill (1990 and 1991A) and Enserch Environmental (1994A and 1994B)
- Appendix B - Geologic Logs, Monitoring Point Installation Records, Monitoring Point/Well Development and Sampling Records, Slug Testing Results, and Survey Data
- Appendix C - Laboratory Analytical Data
- Appendix D - Model Input Parameters and Related Calculations
- Appendix E - Model Input and Output Files
- Appendix F - Remedial Alternative Cost Calculations

TABLE OF CONTENTS (Continued)

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
2.1	Monitoring Point, Soil Borehole, and Monitoring Well Completion Data.....	2-4
2.2	Analytical Protocol for Groundwater, Soil, and Sediment Samples	2-8
3.1	Water Level Data.....	3-7
4.1	Petroleum Product Analysis Results.....	4-4
4.2	1995 Soil and Sediment Data for Fuel-Related Compounds	4-7
4.3	Soil Total Organic Carbon Results	4-9
4.4	1995 Groundwater Quality Data for Fuel-Related Compounds and TOC.....	4-11
4.5	1995 Groundwater Quality Data for Chlorinated Volatile Organic Compounds and Ethylene	4-16
4.6	Coupled Oxidation Reactions for BTEX Compounds.....	4-18
4.7	1995 Groundwater Geochemical Data.....	4-21
4.8	Mass Ratio of Alkalinity (As CaCO_3) Produced to BTEX Degraded During Aerobic Respiration, Denitrification, Iron (III) Reduction, and Sulfate Reduction.....	4-32
4.9	Expressed Assimilative Capacity of Site Groundwater	4-34
5.1	Representative First-Order Anaerobic Decay Rate Constants.....	5-10
5.2	Bioplume II Model Input Parameters.....	5-12
5.3	Calculation of Retardation Coefficients.....	5-21
6.1	Point-of-Compliance Remediation Goals for Groundwater	6-9
6.2	Initial Technical Implementability Screening of Technologies and Process Options for Groundwater Remediation.....	6-11
6.3	Alternative 1 - Cost Estimate.....	6-20
6.4	Alternative 2 - Cost Estimate.....	6-23
6.5	Alternative 3 - Cost Estimate.....	6-25
6.6	Summary of Remedial Alternatives Evaluation Groundwater Remediation.....	6-27
7.1	Long-Term Groundwater Monitoring Analytical Protocol	7-6
7.2	Point-of-Compliance Groundwater Monitoring Analytical Protocol.....	7-8

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.1	Regional Location of Base	1-4
1.2	Site Location and Regional Topography	1-5
1.3	Site Layout	1-7
2.1	Cross Section of Geoprobe®	2-3
2.2	Monitoring Point, Soil Borehole, and Sediment Sample Locations.....	2-5
3.1	Hydrogeologic Cross-Section Location Map	3-4

TABLE OF CONTENTS (Continued)

LIST OF FIGURES (CONTINUED)

<u>No.</u>	<u>Title</u>	<u>Page</u>
3.2	Hydrogeologic Cross-Section A-A'	3-5
3.3	Hydrogeologic Cross Section B-B'	3-6
3.4	Groundwater Elevations March 1995	3-8
3.5	Groundwater Elevations and Point Locations August 1995	3-9
3.6	Groundwater Elevations October 1995	3-10
4.1	Estimated Extent of Free Product 1989 and 1995	4-2
4.2	Soil Headspace Screening Results June 1989	4-5
4.3	Total BTEX Concentrations in Soil and Sediment.....	4-6
4.4	Total BTEX Isopleths for Groundwater March 1995	4-13
4.5	Dissolved Oxygen Isopleths for Groundwater March 1995	4-23
4.6	Ferrous Iron Isopleths for Groundwater March 1995	4-25
4.7	Sulfate Isopleths for Groundwater March 1995	4-27
4.8	Methane Isopleths for Groundwater March 1995	4-29
4.9	Redox Potential Isopleths Groundwater March 1995	4-31
4.10	Anaerobic Reductive Dehalogenation	4-36
4.11	Aerobic Degradation	4-38
5.1	Model Grid Superimposed on Dissolved BTEX Isopleths March 1995	5-4
5.2	Calibrated Groundwater Surface	5-15
5.3	Locations of Simulated Injection Wells	5-17
5.4	Initial Calibrated BTEX Plume.....	5-18
5.5	Model Sensitivity to Variations in Transmissivity	5-23
5.6	Model Sensitivity to Variations in Retardation Coefficient	5-24
5.7	Model Sensitivity to Variations in Anaerobic Decay Rate Constant	5-25
5.8	Model Sensitivity to Variations in Dispersivity	5-26
5.9	Model Sensitivity to Variations in Injected BTEX Concentrations.....	5-27
5.10	Calibrated BTEX Plume.....	5-30
5.11	Simulated Maximum BTEX Concentrations Model OT 24A	5-34
5.12	Simulated Plume Migration Model OT 24A	5-35
5.13	Simulated Maximum BTEX Concentrations Models OT 24A and OT 24B	5-36
5.14	Simulated Plume Migration Model OT 24B.....	5-37
5.15	Simulated Maximum BTEX Concentrations Models OT 24A, OT 24B, and OT 24C	5-39
7.1	Proposed Locations of Plume Definition, Long-Term Monitoring and Point of Compliance Monitoring Wells	7-2

EXECUTIVE SUMMARY

This report presents the results of an intrinsic remediation treatability study (TS) performed by Parsons Engineering Science, Inc. (Parsons ES) at Site OT 24, MacDill Air Force Base (AFB, the Base), Tampa, Florida to evaluate the use of intrinsic remediation (natural attenuation) with long-term monitoring (LTM) as a remedial option for dissolved benzene, toluene, ethylbenzene, and xylenes (BTEX) contamination in the shallow saturated zone. Soil and groundwater contamination is documented for the site, with contamination being present in the aqueous (i.e., dissolved) and gaseous phases and as residual light nonaqueous-phase liquid (LNAPL) within the aquifer matrix. The presence of mobile LNAPL (free product) in the immediate vicinity of the contamination source area is also indicated at this site. This study focused on the impact of dissolved BTEX on the shallow groundwater system at and downgradient from the site. The impact of dissolved chlorinated aliphatic hydrocarbons (CAHs) such as vinyl chloride on the shallow groundwater system is also discussed. Site history and the results of soil, groundwater, and sediment investigations conducted previously also are summarized in this report.

Comparison of BTEX, electron acceptor, and biodegradation byproduct isopleth maps for groundwater at Site OT 24 provides strong qualitative evidence of biodegradation of BTEX compounds. Geochemical data strongly suggest that biodegradation of fuel hydrocarbons is occurring at the site, primarily via the anaerobic processes of sulfate reduction and methanogenesis.

An important component of this study was an assessment of the potential for contamination in groundwater to migrate from the source area to potential receptors at concentrations above regulatory levels intended to be protective of human health and the environment. The Bioplume II model was used to estimate the rate and direction of dissolved BTEX movement through the shallow saturated zone under the influence of advection, dispersion, sorption, and biodegradation. Input parameters for the Bioplume II model were obtained from existing site characterization data, supplemented with data collected by Parsons ES. Model parameters that were not measured at the site were estimated using reasonable literature values.

The results of this study suggest that dissolved BTEX contamination present in groundwater poses no significant threat to human health or the environment in its present, or predicted future, concentrations and distribution. However, dissolved BTEX concentrations in excess of state groundwater quality guidelines for no further action may persist in the vicinity of the site for approximately 21 years (calendar year 2016) without the implementation of an engineered remedial action. If a source removal technology such as *in situ* bioventing is implemented, then dissolved BTEX concentrations may decrease below no-further-action guidelines after 17 years. If limited pumping of groundwater in the plume "hotspot" is performed in combination with source removal, then dissolved BTEX concentrations may decrease below no-further-action guidelines after 13 years. It is the Air Force's opinion that intrinsic remediation with LTM and institutional controls achieves the best combination of risk reduction and cost effectiveness, and recommends that this option be implemented for

this site. Available data suggest that this option will also be suitable for the CAHs dissolved in groundwater. However, engineered source reduction, with or without limited groundwater pumping, should be considered as a contingency in the event that land use in this area changes to commercial or residential, if contaminated groundwater reaches a downgradient surface discharge area such as the mangrove swamp, or if measured BTEX reductions in the groundwater are substantially slower than predicted by the Bioplume model.

To verify the Bioplume II model predictions, the Air Force recommends using five LTM wells and three point-of-compliance (POC) monitoring wells to monitor the long-term migration and degradation of the dissolved BTEX and CAH plumes. Regular sampling and analysis of groundwater from these wells will allow the effectiveness of intrinsic remediation to be monitored, and should allow sufficient time to implement additional engineering controls to contain the plume if BTEX compounds are detected in the POC wells at levels of concern. Up to four plume definition wells should be installed and sampled prior to finalization of the LTM plan to better define the downgradient extent of the dissolved contaminant plume. The results from these wells should be used to optimize the locations of downgradient LTM and POC wells.

Contaminant fate and transport model results indicate that sampling should continue on an annual basis for approximately 10 years, followed by biannual sampling for an additional 16 years. Along with other analyses used to verify the effectiveness of intrinsic remediation, the groundwater samples should be analyzed for both aromatic and halogenated volatile organic compounds (VOCs) by US Environmental Protection Agency (USEPA) methods SW8260 or SW8021. If BTEX concentrations in groundwater from the POC wells exceed the Florida Department of Environmental Protection guidelines of 50 micrograms per liter ($\mu\text{g/L}$) for benzene and total BTEX, or if CAH concentrations exceed applicable action levels, then additional corrective actions may be required to remediate groundwater at the site.

SECTION 1

INTRODUCTION

This report was prepared by Parsons Engineering Science, Inc. (Parsons ES) and presents the results of a treatability study (TS) conducted to evaluate the use of intrinsic remediation for remediation of fuel-hydrocarbon-contaminated groundwater at Site OT 24, the Energy Management Test Laboratory (EMTL), at MacDill Air Force Base (AFB, the Base), Tampa, Florida. Previous investigations determined that fuel hydrocarbons had been released into the soil and shallow groundwater at the site.

The main emphasis of the work described herein was to evaluate if naturally occurring attenuation mechanisms would be sufficient to reduce dissolved fuel-related compounds in groundwater to levels that meet state-specified groundwater protection standards. In addition, the natural attenuation of chlorinated solvents dissolved in the groundwater was qualitatively evaluated. This study is not intended to be a contamination assessment report or a remedial action plan; rather, it is provided for the use of the Base and its prime environmental contractor(s) as information to be used for future decision making regarding this site.

1.1 SCOPE AND OBJECTIVES

Parsons ES was retained by the United States Air Force Center for Environmental Excellence (AFCEE) to conduct site characterization and groundwater modeling to evaluate if intrinsic remediation with long-term monitoring (LTM) would be a scientifically defensible remedial option for contaminated groundwater at Site OT 24.

As used throughout this report, the term "intrinsic remediation" refers to a management strategy that relies on natural attenuation mechanisms to control exposure of potential receptors to concentrations of contaminants in the subsurface that exceed regulatory levels intended to be protective of human health and the environment. "Natural attenuation" refers to the physical, chemical, and biological processes (e.g., sorption, dispersion, and biodegradation) that facilitate intrinsic remediation.

The intent of the intrinsic remediation demonstration program sponsored by AFCEE is to develop a systematic process for scientifically investigating and documenting naturally occurring subsurface attenuation processes that can be factored into overall site remediation plans. The objective of the program and this specific MacDill AFB study is to provide solid evidence of intrinsic remediation of dissolved fuel hydrocarbons in groundwater so that this information can be used by the Base and its prime environmental contractor(s) to develop an effective groundwater remediation strategy. As a result, these studies are not necessarily intended to fulfill specific federal or state requirements regarding site assessments, remedial action plans, or other

such mandated investigations and reports. A secondary goal of this multi-site initiative is to provide a database from multiple sites that demonstrates that natural processes of contaminant degradation often can reduce contaminant concentrations in groundwater to below acceptable cleanup standards before potential receptor exposure pathways are completed.

The scope of work for this project involved the following tasks:

- Reviewing existing hydrogeologic and soil and groundwater quality data for the site;
- Conducting supplemental site characterization activities to determine the nature and extent of soil and groundwater contamination and to collect geochemical data in support of intrinsic remediation;
- Developing a conceptual hydrogeologic model of the shallow saturated zone, including the current distribution of contaminants;
- Determining if natural processes of contaminant attenuation and destruction are occurring in groundwater at the site;
- Simulating the fate and transport of fuel hydrocarbons [benzene, toluene, ethylbenzene, and xylenes (BTEX)] in groundwater under the influence of advection, dispersion, adsorption, and biodegradation using the Bioplume II model;
- Evaluating a range of model input parameters to determine the sensitivity of the model to those parameters and to consider several contaminant fate and transport scenarios;
- Determining if natural processes are sufficient to minimize BTEX plume expansion so that groundwater quality standards can be met at a downgradient point of compliance (POC);
- Developing remedial action objectives (RAOs) and reviewing available remedial technologies;
- Using the results of modeling to recommend the most appropriate remedial option based on specific effectiveness, implementability, and cost criteria; and
- Providing a LTM plan that includes LTM and POC well locations and a sampling and analysis plan (SAP).

Much of the hydrogeologic and groundwater chemical data necessary to evaluate the various remedial options were available from previous investigations conducted at this site or at other sites with similar characteristics, or in the technical literature. The field work conducted under this program was oriented toward the collection of supplementary hydrogeologic and chemical data necessary to document and model the effectiveness of intrinsic remediation with LTM for fuel-hydrocarbon-contaminated groundwater. Site characterization activities in support of intrinsic remediation,

performed in March and April 1995, included use of the Geoprobe® system for soil sample collection and groundwater monitoring point installation; aquifer testing; and sampling and analysis of groundwater from newly installed monitoring points and existing monitoring wells. In addition, seven groundwater monitoring points were manually installed in the surficial aquifer using a post-hole driver or electric hammer.

Site-specific data were used to develop a fate and transport model for the site using the groundwater flow and solute transport model Bioplume II, and to conduct a preliminary exposure pathways analysis. The Bioplume II model was used to simulate the movement of dissolved BTEX in the shallow saturated zone under the influence of advection, dispersion, sorption, and biodegradation. Model results were used to help assess the potential for completion of receptor exposure pathways involving groundwater and to identify whether intrinsic remediation with LTM is an appropriate and defensible remedial option for contaminated groundwater.

This report contains nine sections, including this introduction, and six appendices. Section 2 summarizes site characterization activities. Section 3 summarizes the physical characteristics of the study area. Section 4 describes the nature and extent of soil and groundwater contamination and the geochemistry of soil and groundwater at the site. Section 5 describes the Bioplume II model and design of the conceptual model for the site, lists model assumptions and input parameters, and describes sensitivity analyses, model output, and the results of the Bioplume II modeling. Section 6 presents a limited comparative analysis of remedial alternatives. Section 7 presents the LTM plan for the site. Section 8 presents the conclusions of this work and provides recommendations for further work at the site. Section 9 lists the references used to develop this document. Appendix A contains pertinent figures and tables summarizing data collected during the previous site investigations (CH2M Hill, 1990 and 1991a; Enserch Environmental, 1994a and 1994b). Appendix B contains Geoprobe® borehole logs, monitoring point installation diagrams, development and sampling records, aquifer slug test results, and survey data. Appendix C presents soil and groundwater analytical results. Appendix D contains calculations and model input parameters, and Appendix E contains Bioplume II model input and output in American Standard Code for Information Interchange (ASCII) format on a diskette. Appendix F contains remedial alternative design and cost calculations.

1.2 FACILITY AND SITE BACKGROUND

The Base, located on the southernmost tip of the Interbay Peninsula, covers nearly 7,000 acres in Hillsborough County, Florida, immediately south of the city of Tampa (Figure 1.1). The Base, which was established in the early 1950's, is bordered on the north by Tampa, on the east by Hillsborough Bay, and on the south and west by Tampa Bay.

Site OT 24, which is located near the western edge of the Base adjacent to the bulk fuel storage tank farm (Figure 1.2), has been a fuel testing laboratory used for quality control testing of petroleum fuels since the early 1950s (CH2M Hill, 1990). Figure 1.3 presents the layout of this site. Wastewater from equipment cleaning and fuel testing activities was routinely disposed of in sink drains located within the EMTL. Two drain fields located in a grassy area south of the laboratory received the laboratory wastewater, along with sanitary wastes. Prior to discharge, wastewater was first routed

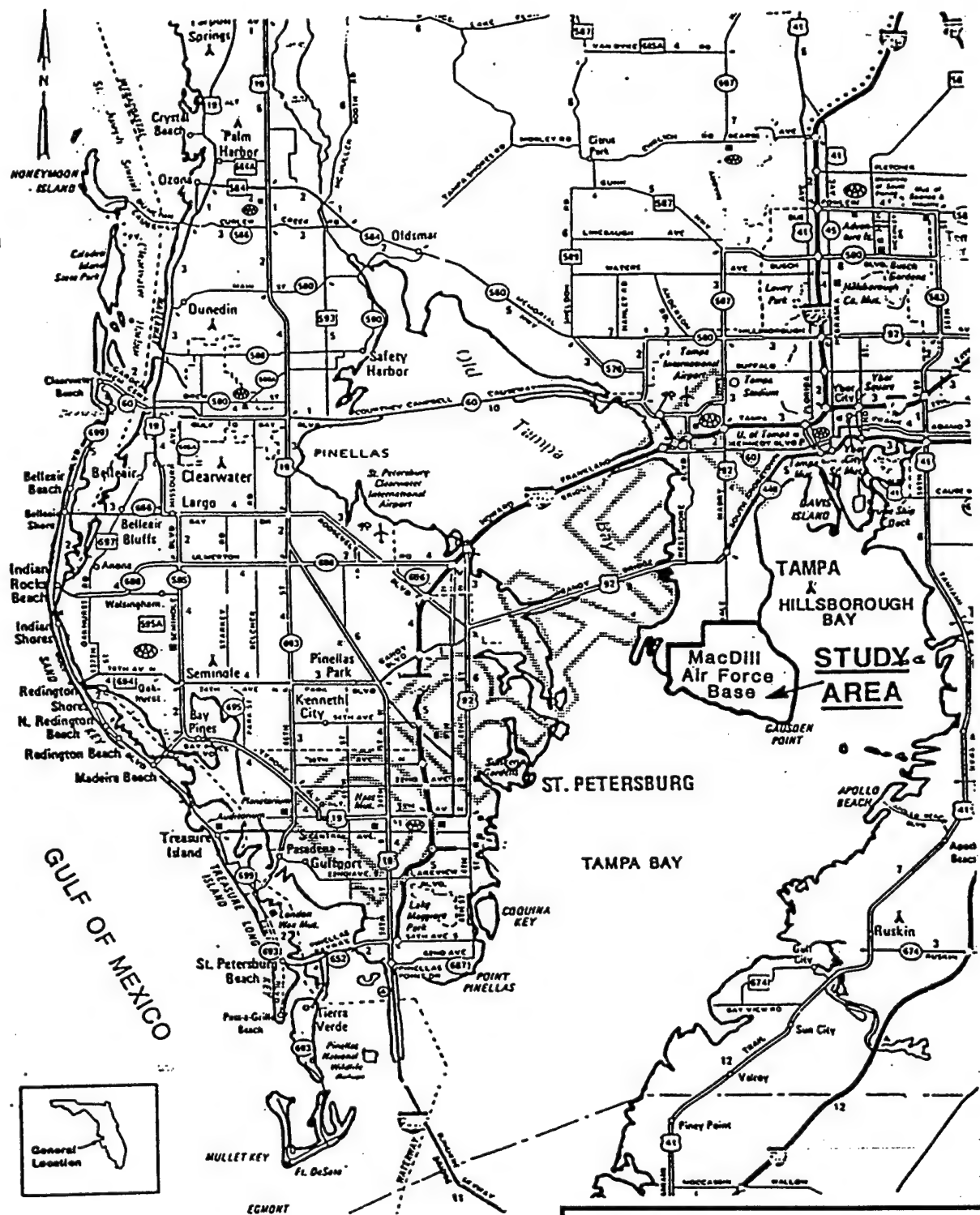


FIGURE 1.1

REGIONAL LOCATION OF BASE

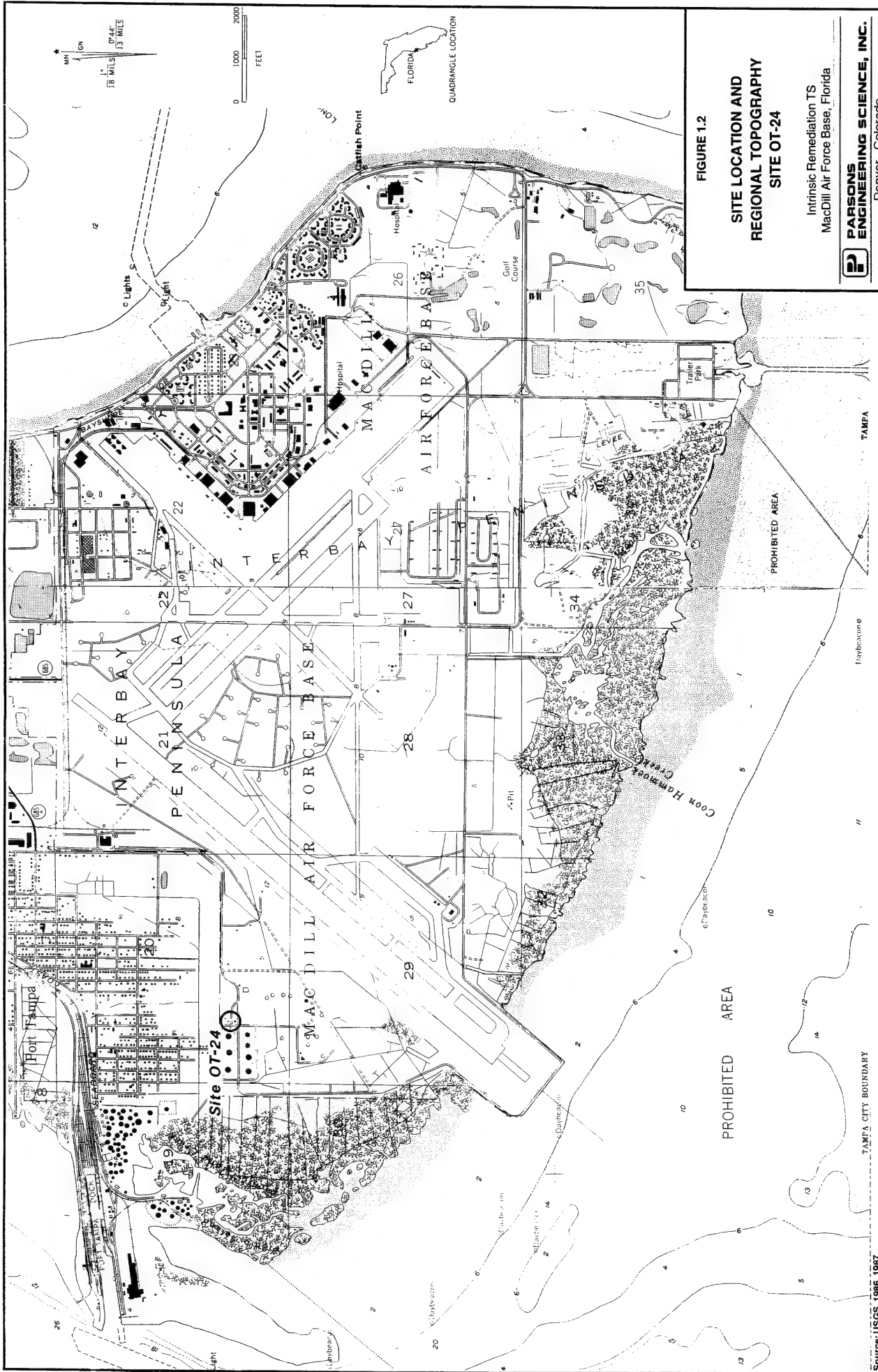
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Sources: CH₂ M HILL, 1991B



Source: USGS, 1986, 1987

FIGURE 1.2

**SITE LOCATION AND
REGIONAL TOPOGRAPHY
SITE OT-24**

Intrinsic Remediation TS
MacDill Air Force Base, Florida

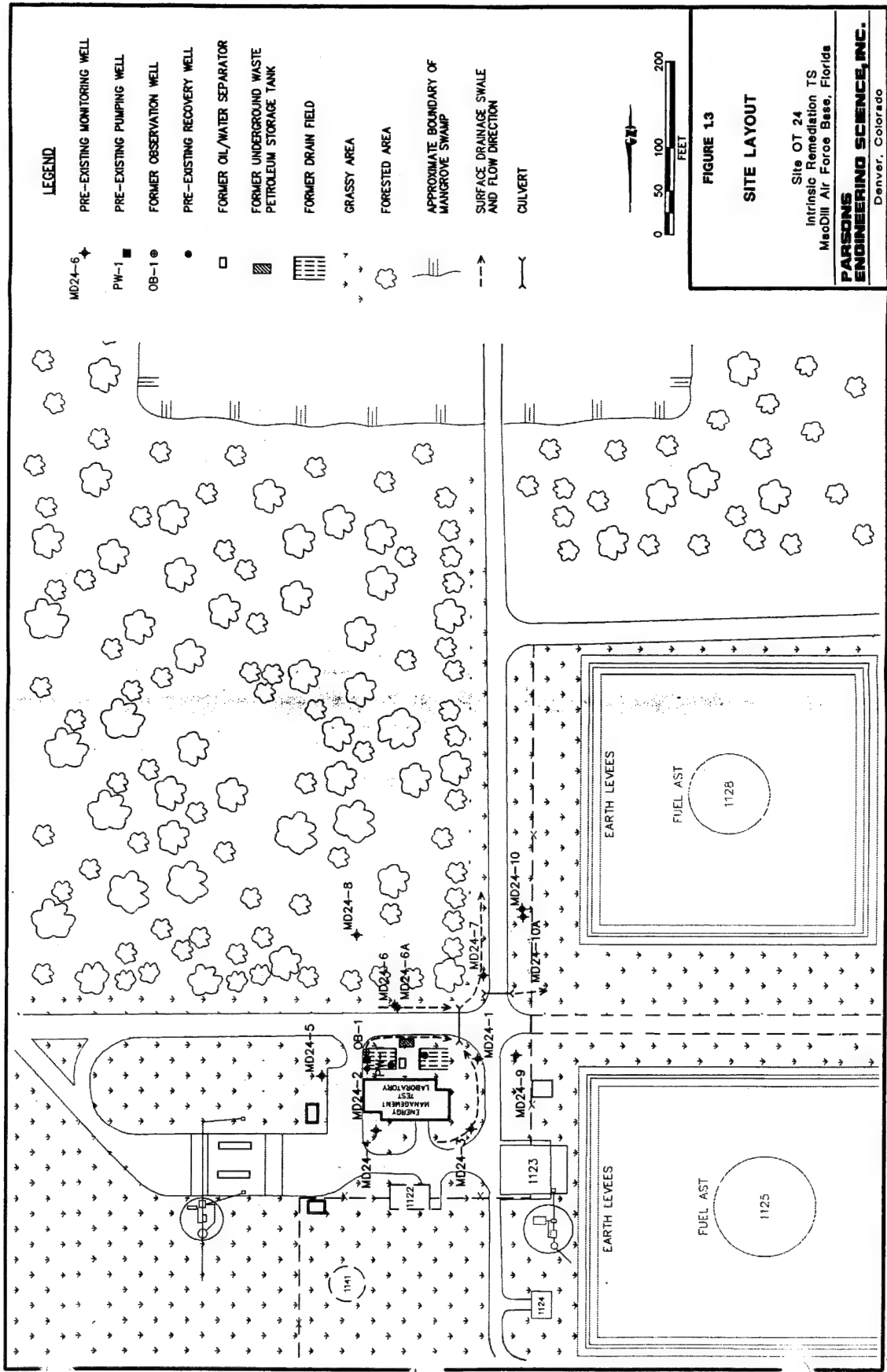
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to an oil/water separator located adjacent to the west side of the eastern drain field, and then discharged to the eastern drain field. Undissolved petroleum product collected from the oil/water separator was stored in an underground storage tank (UST) located between the two drain fields. Since March 1989, all wastewater generated from fuel testing or equipment cleanup has been contained and transported offsite for disposal. Sanitary wastes were discharged to the eastern drain field until its removal late in 1991. Potential sources of contamination at Site OT 24 include the two drain fields, the former oil/water separator, and the former waste petroleum UST (Figure 1.3).

Installation Restoration Program (IRP) action was initiated at the site in 1988 when the Hazardous Waste Remedial Actions Program (HAZWRAP) retained CH2M Hill to conduct a contamination assessment of Site OT 24. The Site OT 24 preliminary contamination assessment, conducted in November 1988, involved the installation of four shallow monitoring wells (MD 24-1 through MD 24-4). In April 1989, three piezocone soundings were conducted to depths ranging from 28 to 50 feet below ground surface (bgs) to determine the thickness of the surficial aquifer in the vicinity of the facility. In addition, 12 Hydrocone® groundwater samples were collected at depths ranging from 7 to 18 feet bgs to further evaluate the horizontal and vertical extent of dissolved contamination as well as the hydraulic properties of the aquifer. Ten temporary well points (TP-1 through TP-10) were installed to depths ranging from 5 to 9 feet bgs and sampled in May 1989 to better define the horizontal extent of the dissolved contaminant plume. Results from these temporary well samples were used to locate six additional monitoring wells in August 1989 (MD 24-5 through MD 24-10) (CH2M Hill, 1990).

A pumping test well (PW-1) and an observation well (OW-1) were installed in July 1989 to conduct an aquifer pumping test at the site. Well PW-1 was screened from 10 to 20 feet bgs. In August 1989, a 48-hour aquifer pumping test was performed to determine the hydraulic characteristics of the surficial aquifer. Slug tests were also performed in monitoring wells MD24-1 through MD24-7, MD24-9, MD24-10, and the pumping test observation well to evaluate the lateral distribution of the aquifer hydraulic conductivity. Ten temporary piezometers (P-1 through P-10) were installed in September 1989 to determine the areal extent of mobile, light nonaqueous-phase liquid (LNAPL) (free product) on the groundwater surface.

Groundwater samples were collected in December 1988, April 1989, May 1989, and August 1989 from monitoring wells and temporary well points located at the site. In December 1988, fluid in the waste petroleum UST was also sampled. The samples were analyzed for volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), pesticides/polychlorinated biphenyls (PCBs), and inductively coupled plasma spectrometry (ICP) metals plus arsenic, selenium, mercury, and antimony. During April and May 1989, a groundwater sample from well MD24-4 was analyzed for total chromium, and Hydrocone® samples and samples from temporary well points TP-9 and TP-10 were analyzed for chlorinated and/or aromatic VOCs. Also in May 1989, samples from wells MD24-1 and MD24-2 and temporary well points TP-1 through TP-8 were analyzed for aromatic VOCs. In August 1989, samples from wells MD24-1 through MD24-10 were analyzed for VOCs, SVOCs, and lead (CH2M Hill, 1990).



LEGEND

- MD24-6
- PRE-EXISTING MONITORING WELL
- PW-1
- PRE-EXISTING PUMPING WELL
- OB-1
- FORMER OBSERVATION WELL
- PRE-EXISTING RECOVERY WELL
- FORMER OIL/WATER SEPARATOR
- FORMER UNDERGROUND WASTE PETROLEUM STORAGE TANK
- FORMER DRAIN FIELD
- GRASSY AREA
- FORESTED AREA
- APPROXIMATE BOUNDARY OF MANGROVE SWAMP
- SURFACE DRAINAGE SWALE AND FLOW DIRECTION
- CULVERT

FIGURE 13

SITE LAYOUT

Site OT 24
Intrinsic Remediation TS
MacDill Air Force Base, Florida

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Twelve soil samples and seven sediment samples were collected at Site OT-24 during the CH2M Hill (1990) investigation. The sediment samples were collected from shallow drainage swales at the site. All samples were screened in the field for total hydrocarbons using a flame ionization detector (FID), and four of the samples were analyzed at a laboratory for VOCs, total recoverable petroleum hydrocarbons (TRPH), and total chromium, arsenic, cadmium, and lead.

The results of the CH2M Hill (1990) investigation are documented in the Contamination Assessment Report (CAR). Pertinent figures and tables from the CAR are reproduced in Appendix A of this document. Groundwater analytical results indicated the presence of total dissolved BTEX contamination at concentrations up to 225 micrograms per liter ($\mu\text{g/L}$) migrating from the site toward the southwest. During the pumping test, analysis of discharge water samples detected total BTEX concentrations ranging from 1,210 to 1,710 $\mu\text{g/L}$, indicating that the analytical results for the monitoring well samples were not representative of the maximum dissolved BTEX concentrations present in the surficial aquifer. The investigation also detected the presence of a mobile LNAPL plume at the site, and petroleum-hydrocarbon-contaminated soils and sediments were encountered south of the facility.

Several nonfuel-related VOCs were also detected in groundwater samples collected by CH2M Hill (1990). These VOCs (and the maximum detected concentrations) included methylene chloride (29 $\mu\text{g/L}$), acetone (19 $\mu\text{g/L}$), carbon disulfide (2 $\mu\text{g/L}$), vinyl chloride (59 $\mu\text{g/L}$), 1,1-dichloroethane (1,1-DCA) (178 $\mu\text{g/L}$), 2-butanone (25 $\mu\text{g/L}$), and chloromethane (1 $\mu\text{g/L}$). The VOCs vinyl chloride and 1,1-DCA also were detected in the pumping test discharge water at maximum concentrations of 23 $\mu\text{g/L}$ and 26 $\mu\text{g/L}$, respectively. The maximum concentrations of vinyl chloride and 1,1-DCA were detected in the Hydrocone® samples obtained in 1989, with the highest concentrations occurring adjacent to the former waste petroleum UST and near monitoring well MD24-6 (Figure 1.3). Concentrations of these two VOCs detected in groundwater samples from monitoring wells have been substantially lower. The maximum concentrations of vinyl chloride and 1,1-DCA detected in monitoring well samples were 16.4 $\mu\text{g/L}$ and 7.1 $\mu\text{g/L}$, respectively.

As a result of comments on the CAR by the Florida Department of Environmental Regulation (FDER), two additional deep monitoring wells, MD 24-6A and MD 24-10A (Figure 1.3), were installed in September 1990 to further evaluate the vertical extent of contamination. The primary constituents of concern prompting these installations were vinyl chloride and 1,1-DCA. The 10 existing monitoring wells were also sampled again. The results of the additional investigation indicated that the horizontal and vertical extent of the contamination had been adequately determined, and a Contamination Assessment Report Addendum (CARA) was submitted by CH2M Hill (1991a) in April 1991.

In May 1991, a *Remedial Action Plan for Site OT 24* (CH2M Hill, 1991b) was submitted to the state. Subsequently, a groundwater and mobile LNAPL recovery system consisting of two pumping wells was installed, and the oil/water separator, drain fields, and waste petroleum UST were removed. During the removal process, which occurred late in 1991, approximately 1,200 cubic yards of contaminated soil south of the EMTL were excavated and removed from the site. The excavation area included the majority of the grassy area between the EMTL and the road to the south

(Figure 1.3), and the majority of the contaminated soils was removed (Jackson, 1995). During the excavation, mobile LNAPL was encountered on the groundwater surface, and some product removal was accomplished. The groundwater and LNAPL recovery system designed and installed by CH2M Hill was never operated, and is currently not operational.

Additional groundwater sampling rounds were performed at Site OT 24 by Enserch Environmental (1994a and 1994b) in May and August 1994. The maximum total BTEX concentration detected in these samples was 160 µg/L in monitoring well MD24-6. Low levels of chlorinated VOCs (less than 3 µg/L) were also detected in groundwater samples (Appendix A). The site-specific data presented in Sections 3, 4, and 5 are based on reviews of the documents referenced above and on data collected by Parsons ES under this program.

SECTION 2

SITE CHARACTERIZATION ACTIVITIES

This section presents the methods used by Parsons ES personnel to collect site-specific data at Site OT 24, MacDill AFB, Florida. To meet the requirements of the intrinsic remediation demonstration, additional data were required to evaluate near-surface geology and geochemistry, aquifer properties, and the extent of soil and groundwater contamination. Site characterization activities involved using the Geoprobe® system for soil sampling and groundwater monitoring point placement. In addition, selected monitoring points were manually driven into the surficial aquifer using a post-hole driver or electric hammer. The term "monitoring point" is used in this report to distinguish these groundwater monitoring stations from conventionally-constructed monitoring wells. Groundwater sampling was accomplished during this investigation at newly installed monitoring points and pre-existing monitoring wells. Two aquifer slug tests were conducted at previously installed wells MD24-4 and MD24-10A.

The physical and chemical data listed below were collected during the field work phase of the TS:

- Depth from measurement datum to the water table in monitoring wells and monitoring points;
- Stratigraphy of subsurface media;
- Hydraulic conductivity as determined from slug test data;
- Groundwater geochemical data [pH, temperature, electrical conductivity, total alkalinity, reduction/oxidation (redox) potential, dissolved oxygen (DO), chloride, nitrate, nitrite, ammonia, ferrous and total iron, sulfate, sulfide, manganese, ammonia, carbon dioxide, total organic carbon (TOC), and methane];
- Concentrations of chlorinated and aromatic VOCs, total volatile (gasoline-range) petroleum hydrocarbons (TVH), and ethylene in groundwater;
- Concentrations of aromatic VOCs, TVH, total extractable petroleum hydrocarbons (TEH), and TOC in soil; and
- Concentrations of aromatic VOCs, TVH, and TEH in sediment.

The following sections describe the procedures that were followed when collecting site-specific data. Additional details regarding investigative activities are presented in the TS work plan (Parsons ES, 1995a).

2.1 GEOPROBE®, SOIL AND SEDIMENT SAMPLING AND MONITORING POINT INSTALLATION

Geoprobe®-related field work occurred between March 8 and March 11, 1995, and consisted of soil sampling and groundwater monitoring point installation of monitoring points 24MP-1S through 24MP-10D. These activities were performed according to the procedures described in the work plan (Parsons ES, 1995a) and summarized in the following sections.

The Geoprobe® system is a hydraulically powered percussion/probing machine used to advance sampling tools through unconsolidated soils. This system provides for the rapid collection of soil, soil gas, and groundwater samples at shallow depths while minimizing the generation of investigation-derived waste materials. Figure 2.1 is a diagram of the Geoprobe® system.

2.1.1 Groundwater Monitoring Point Locations and Completion Intervals

Twenty new groundwater monitoring points were installed at 11 locations in March 1995 to assist in the characterization of the contaminant distribution and the shallow groundwater flow system at Site OT 24. These points are identified as 24MP-1S, 24MP-1D, 24MP-2S, 24MP-2D, 24MP-3S, 24MP-3D, 24MP-4S, 24MP-5S, 24MP-5D, 24MP-6S, 24MP-7S, 24MP-7D, 24MP-8S, 24MP-8D, 24MP-9S, 24MP-9D, 24MP-10S, 24MP-10D, 24PZ-1S, and 24PZ-1D. The latter two points, 24PZ-1S/1D, were not installed using the Geoprobe®, but were manually driven to depth with a post-hole driver. Five additional monitoring points were installed at four locations in July 1995 to better delineate the downgradient extent of the dissolved BTEX plume and groundwater flow directions south of the Energy Management Test Laboratory. These points (24PZ-2S, 24PZ-3S, 24PZ-3D, 24PZ-4S, and 24PZ-5S) were manually driven to depth using a post-hole driver or electric hammer. The new monitoring points were installed at the locations shown on Figure 2.2, and Table 2.1 presents completion details. Nested points (e.g., 24MP-1S and 24MP-1D) were installed adjacent to each other, with one point (designated by the suffix "S") screened across the water table, and the other point (designated by the suffix "D") screened approximately 10 to 14 feet below the bottom of the shallow point. The monitoring point locations were selected to provide the hydrogeologic and chemical data necessary for successful implementation of the Bioplume II model and to support the intrinsic remediation demonstration. Two soil boreholes, 24SS-1 and 24SS-3 (Figure 2.2), were advanced using the Geoprobe® for soil sampling purposes; groundwater monitoring points were not installed in these boreholes.

2.1.2 Groundwater Monitoring Point Placement and Soil Sampling Procedures

2.1.2.1 Geoprobe® Clearance Activities

All subsurface utility lines and other manmade subsurface features were located, and proposed monitoring point and soil borehole locations were cleared and approved by

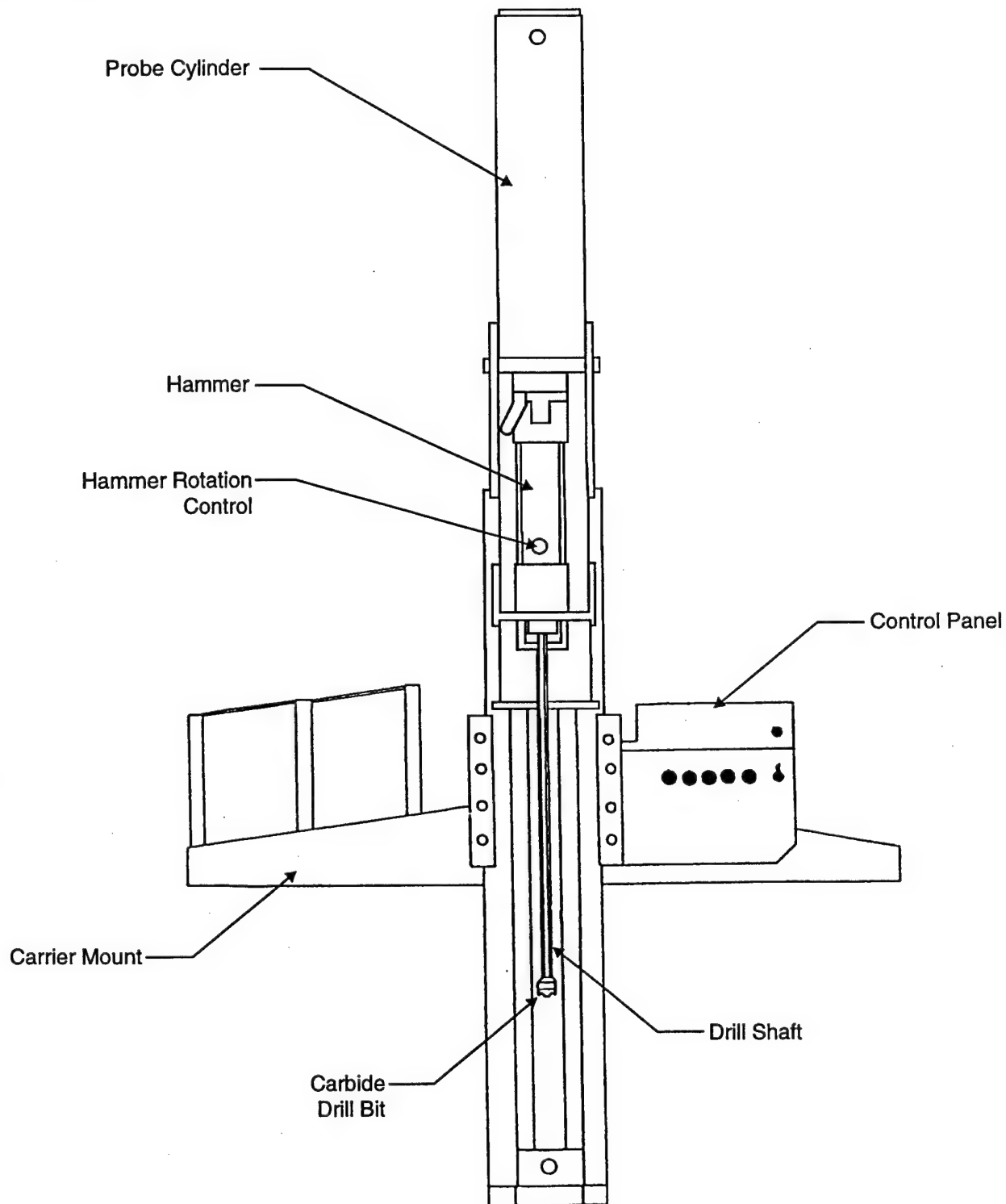


FIGURE 2.1

**CROSS-SECTION
OF GEOPROBE®**

Site OT 24
Intrinsic Remediation TS
MacDill Air Force Base, Florida



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TABLE 2.1
MONITORING POINT, SOIL BOREHOLE, AND MONITORING WELL COMPLETION DATA
SITE 0T 24
INTRINSIC REMEDIATION TS
MACDILL AFB, FLORIDA

Well/Borehole Identification	Installation Date	Northing	Easting	Well Diameter (Inches)	Borehole Diameter (Inches)	Total Depth (Feet bgs) ^u	Sandpack Interval (Feet bgs)	Screened Interval (Feet bgs)	Elevation toc (Feet msl) ^v	Elevation Ground (Feet msl)
New Monitoring Points										
24MP-1S	3/8/95	1279794.735	484712.382	0.5	2.0	6.2	0.5-5.3	3.3-5.3	5.576	5.66
24MP-1D	3/8/95	1279794.735	484712.382	0.375	1.0	18.2	15.5-18.2	17.7-18.2	NM ^w	5.66
24MP-2S	3/8/95	1279782.494	484683.810	0.5	2.0	6.1	0.5-4.0	4.0-6.0	4.943	5.25
24MP-2D	3/8/95	1279782.494	484683.810	0.375	1.0	18.0	0.5-17.5	17.5-18.0	NM	5.25
24MP-3S	3/9/95	1279726.251	484585.675	0.5	2.0	5.2	0.5-3.2	3.2-5.2	3.997	4.17
24MP-3D	3/9/95	1279726.251	484585.675	0.375	1.0	20.0	0.5-19.5	19.5-20.0	NM	4.17
24MP-4S	3/9/95	1279857.983	484852.348	0.5	2.0	5.0	0.5-3.0	3.0-5.0	5.379	5.42
24MP-5S	3/9/95	1279851.201	484594.740	0.5	2.0	5.0	0.5-3.0	3.0-5.0	5.190	5.39
24MP-5D	3/9/95	1279851.201	484594.740	0.375	1.0	18.0	10.0-18.0	17.5-18.0	NM	5.39
24MP-6S	3/10/95	1280097.214	485064.749	0.5	2.0	7.0	0.5-2.0	2.0-7.0	4.496	4.60
24MP-7S	3/10/95	1279685.670	484489.996	0.5	2.0	7.0	0.5-2	2.0-7.0	4.000	4.15
24MP-7D	3/10/95	1279685.670	484489.996	0.375	1.0	17.0	NP ^w	16.5-17.0	NM	4.15
24MP-8S	3/10/95	1279740.830	484465.839	0.5	2.0	7.0	0.5-2	2.0-7.0	4.154	4.26
24MP-8D	3/10/95	1279740.830	484465.839	0.375	1.0	18.0	15.0-17.5	17.5-18.0	NM	4.26
24MP-9S	3/10/95	1279731.613	484668.828	0.5	2.0	7.0	0.5-2.0	2.0-7.0	3.596	3.84
24MP-9D	3/10/95	1279731.613	484668.828	0.375	1.0	18.0	15.0-17.5	17.5-18.0	NM	3.84
24MP-10S	3/10/95	1279729.838	484796.109	0.5	2.0	7.0	0.5-2.0	2.0-7.0	4.196	4.10
24MP-10D	3/11/95	1279729.838	484796.109	0.375	1.0	18.0	NP	17.5-18.0	NM	4.10
24PZ-1S	3/23/95	1279592.764	484693.216	1.38	1.5	6.0	NP	3.0-6.0	6.318	4.96
24PZ-1D	3/23/95	1279591.482	484694.894	1.05	1.25	18.5	NP	17.53-18.53	5.540	4.96
24PZ-2S	7/19/95	1279507.480	484542.498	1.38	1.6	5.5	NP	3.0-5.5	4.160	4.21
24PZ-3S	7/19/95	1279458.895	484621.479	1.38	1.6	5.5	NP	3.0-5.5	3.750	3.73
24PZ-3D	7/20/95	1279461.287	484621.461	1.05	1.25	19.0	NP	18.0-19.0	3.820	3.75
24PZ-4S	7/19/95	1279353.583	484444.316	1.38	1.3	5.5	NP	3.0-5.5	4.430	4.46
24PZ-5S	7/19/95	1279287.887	484588.359	1.38	1.3	5.5	NP	3.0-5.5	4.400	4.53
New Soil Boreholes										
24SS-1	3/10/95	1279797.341	484657.391	NA ^w	2.0	10.0	NA	NA	NA	5.56
24SS-3	3/11/95	NM	NM	NA	2.0	12.0	NA	NA	NA	NM
Pre-Existing Monitoring Wells										
MD 24-1	9/88	1279799.508	484629.381	2	8.0	20.0	8.0-20.0	10.0-20.0	8.879	5.25
MD 24-2	9/88	1279811.123	484752.067	2	8.0	20.0	8.5-20.0	10.0-20.0	8.026	5.57
MD 24-3	9/88	1279875.954	484638.631	2	8.0	20.0	8.0-20.0	10.0-20.0	8.226	5.15
MD 24-4	9/88	1279878.943	484743.387	2	8.0	20.0	7.0-20.0	10.0-20.0	8.506	5.62
MD 24-5	7/89	1279818.832	484801.662	2	8.0	12.0	1.2-12.0	2.0-12.0	4.893	5.11
MD 24-6	7/89	1279740.487	484722.578	2	8.0	12.5	1.5-12.5	2.5-12.5	4.396	4.92
MD 24-6A	7/89	1279743.305	484718.238	2	NR ^v	25.0	19.0-25.0	20.0-25.0	4.699	4.92
MD 24-7	7/89	1279708.038	484626.379	2	8.0	12.2	1.2-12.2	2.2-12.2	4.130	4.10
MD 24-8	7/89	1279663.223	484767.700	2	8.0	12.2	1.5-12.2	2.2-12.2	4.361	4.59
MD 24-9	7/89	1279796.213	484587.781	2	8.0	12.2	1.7-12.2	2.2-12.2	4.534	4.17
24MD-10	7/89	1279634.055	484584.964	2	8.0	12.3	1.3-12.3	2.3-12.3	3.710	3.90
MD 24-10A	7/89	1279641.995	484585.469	2	NR	29.0	23.0-29.0	24.0-29.0	3.657	3.90

^u bgs = below ground surface.

^v toc = top of casing; msl = above mean sea level.

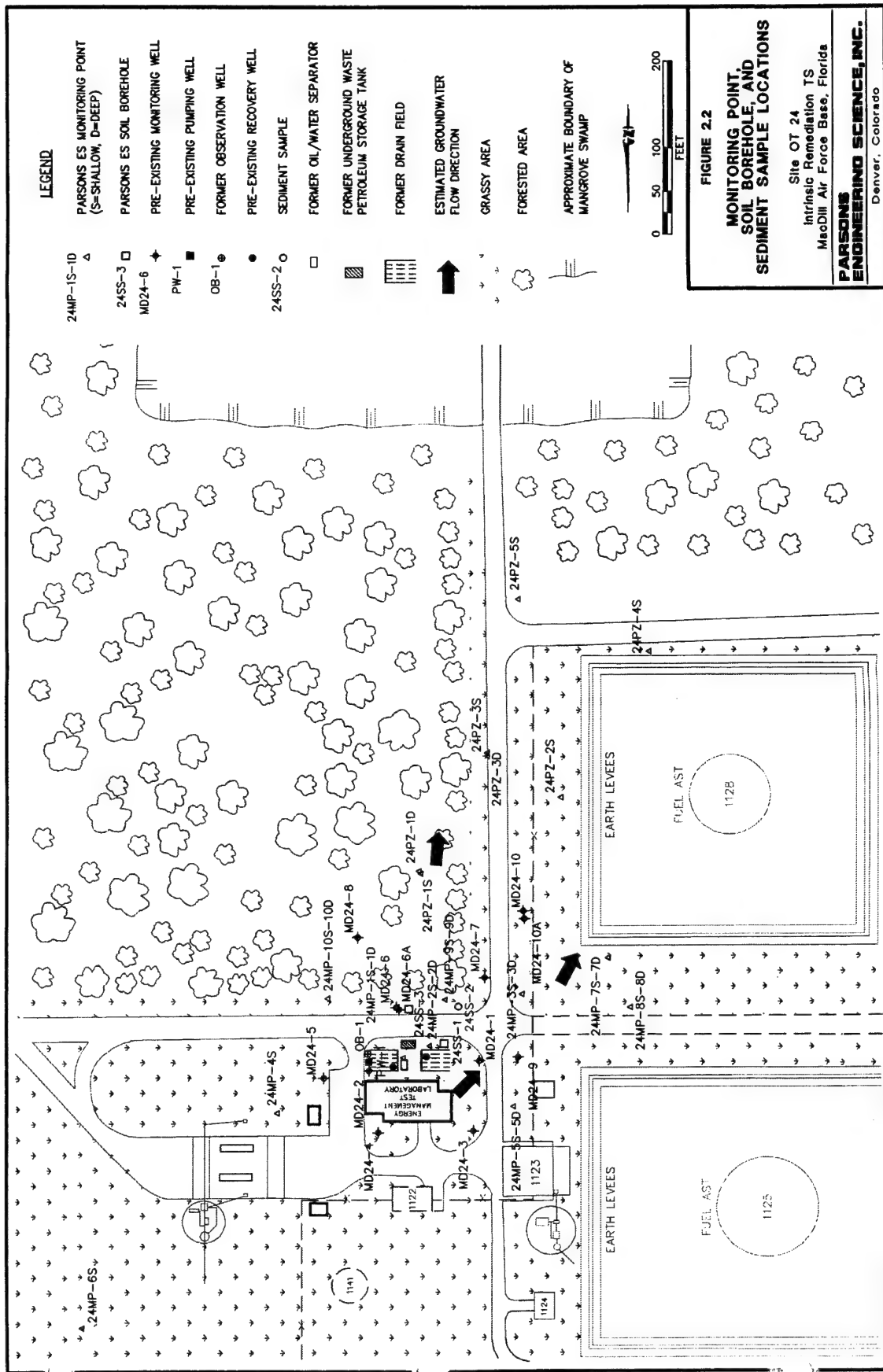
^w NM = not measured.

^w NP = not placed.

^w NA = not applicable.

^v NR = not reported.

Note: All pre-existing monitoring wells were installed by CH2M Hill (1990 and 1991a).



the Base prior to any drilling activities. Water used during Geoprobe® intrusive activities, equipment cleaning, or monitoring point grouting was obtained from an onsite potable water supply.

2.1.2.2 Equipment Decontamination Procedures

Prior to using the Geoprobe® at the site and between each Geoprobe® location, all probe rods, tips, sleeves, pushrods, samplers, tools, and other downhole equipment were decontaminated using an Alconox® detergent and potable water solution followed by a high-pressure potable water wash. All sampling equipment also underwent an additional rinse with isopropyl alcohol, followed by a final rinse with deionized water.

During intrusive activities, the Geoprobe®, probe rods, and any downhole sampling equipment were decontaminated at a site decontamination area. Water from the decontamination operation was collected in 55-gallon drums and was transported to an on-Base oil/water separator for disposal. Precautions were taken to minimize any impact to the area surrounding the decontamination area that might result from the decontamination operations. All decontamination activities were conducted in a manner so that the excess water was controlled and not allowed to flow into any open borehole.

Fuel, lubricants, and other similar substances were handled in a manner consistent with accepted safety procedures and standard operating practices. All monitoring point completion materials were factory-sealed and were not stored near or in areas that could be affected by these substances.

2.1.2.3 Borehole Advancement and Soil/Sediment Sampling

Except for the seven manually driven monitoring points identified in Section 2.1.1, borehole advancement was accomplished using the Geoprobe®. Using this technique, a probe-drive sampler serves as both the driving point and the sample collection device and is attached to the leading end of the probe rods. To advance the borehole and collect a soil sample, the sampler was pushed or driven to the desired sampling depth, and the stop pin was removed, allowing the piston and drive point to retract as the sample barrel was pushed into undisturbed soil. The soil cores were retained within a clear acetate liner inside the sampling barrel. The probe rods were then retracted, bringing the sampling device to the surface. Soil samples were obtained using a 4-foot by 1.5-inch-inside-diameter (ID) and a 2-foot by 1 1/16-inch-ID sampling device. The large sampler was used for the initial 4 feet of soil. The smaller sampler was then advanced for the remainder of the borehole in an attempt to minimize the smearing of shallow contamination into deeper portions of the borehole. Where possible, samples were collected continuously over the full depth of the soil borehole. However, in some instances, the presence of loose, saturated sand below the water table prevented collection of soil samples.

Upon retrieval, the soil sample was extruded from the liner and transferred to analyte-appropriate jars supplied by the analytical laboratory. In addition, a portion of the soil sample was placed in an unused, sealable plastic bag for photoionization detector (PID) headspace measurement of VOCs. Soil remaining in the liner was used for lithologic and stratigraphic logging. Soil samples were not collected during

installation of the manually driven monitoring points (designated with the identifier "PZ").

Bags containing soil samples collected for the headspace screening procedure were quickly sealed and stored for 15 minutes at the ambient temperature. Semiquantitative measurements were made by puncturing the bag seal with the PID probe and reading the concentration of the headspace gases. The PID relates the concentration of total ionizable VOCs in the sample to an isobutylene calibration standard. The PID was also used to monitor for VOCs in the worker breathing zone.

The Parsons ES field hydrogeologist observed drilling and well installation activities and maintained a descriptive log of subsurface materials recovered. Geologic borehole logs are presented in Appendix B. These logs contain:

- Sampled interval (top and bottom depths);
- Presence or absence of contamination based on odor, staining, and/or PID readings;
- Soil description, including color, major textural constituents, minor constituents, relative moisture content, plasticity of fines, cohesiveness, grain size, structure or stratification, and any other significant observations; and,
- Lithologic contacts, with the depth of lithologic contacts and/or significant textural changes recorded to the nearest 0.1 foot.

In almost all cases, one soil sample from the vicinity of the water table was submitted for laboratory analysis. In addition, a deeper sample was generally submitted from each borehole to assess the vertical extent of contamination.

Analyte-appropriate sample containers for fixed-base analysis of the targeted analytes were provided by the subcontracted laboratory, Evergreen Analytical, Inc. (EAL) of Wheat Ridge, Colorado, or by the US Environmental Protection Agency (USEPA) National Risk Management Research Laboratory (NRMRL) of Ada, Oklahoma. A sample label was firmly attached to the container side, and the following information was legibly and indelibly written on the label:

- Sample identification,
- Sample depth,
- Sampling date; and,
- Sample collector's initials.

After the samples were sealed and labeled, they were placed in a cooler with ice and held for overnight transport via Federal Express® to EAL or NRMRL. A summary of the field and fixed-base chemical analyses performed for soil and groundwater samples is presented in Table 2.2. Information regarding sample containers, preservatives, and

TABLE 2.2
ANALYTICAL PROTOCOL FOR
GROUNDWATER, SOIL, AND SEDIMENT SAMPLES
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

MATRIX/PARAMETER	METHOD	ANALYTICAL LABORATORY
WATER		
Total Iron	Colorimetric, Hach Method 8008	Field
Ferrous Iron (Fe+2)	Colorimetric, Hach Method 8146	Field
Ferric Iron (Fe+3)	Difference between total and ferrous iron	Field
Manganese	Colorimetric, Hach Method 8034	Field
Sulfide	Colorimetric, Hach Method 8131	Field
Sulfate	Colorimetric, Hach Method 8051	Field
Sulfate	E300 or SW9056	Evergreen ^{a/}
Nitrate	Titrimetric, Hach Method 8039 and 8192	Field
Nitrate	E300 or SW9056	Evergreen
Nitrite	Titrimetric, Hach Method 8040	Field
Nitrite	E300 or SW9056	Evergreen
Redox Potential	A2580B, direct-reading meter	Field
Oxygen	Direct-reading meter	Field
pH	Direct-reading meter	Field
Conductivity	Direct-reading meter	Field
Temperature	Direct-reading meter	Field
Alkalinity (Carbonate [CO3-2] and Bicarbonate [HCO3-1])	Titrimetric, Hach Method 8221	Field
Carbon Dioxide	CHEMetrics Method 4500	Field
Chloride	Hach Model 8P	Field
Chloride	E300 or SW9056	Evergreen
Ammonia--Diss. Gas in Water	CHEMetrics Method 4500	Field
Alkalinity	310.1	Evergreen
Methane	RSKSOP175	USEPA ^{b/}
Ethene	RSKSOP175	USEPA
Total Organic Carbon	EPA 415.1	Evergreen
Aromatic Hydrocarbons (Including Trimethylbenzene and Tetramethylbenzene)	SW8020	Evergreen
Total Volatile Hydrocarbons	SW8015, modified	Evergreen
Volatile Organics	GS/MS method, SW8240	USEPA
Free Product	GS/MS fuel identification	Evergreen
SOIL/SEDIMENT		
Total Organic Carbon	SW9060, modified	Evergreen ^{c/}
Moisture	EPA 160.3	Evergreen
Aromatic Hydrocarbons	SW8020	Evergreen
Total Volatile and Extractable Hydrocarbons	SW8015, modified	Evergreen

a/ Evergreen Analytical, Inc. of Wheat Ridge, Colorado.

b/ National Risk Management Research Laboratory of Ada, Oklahoma.

c/ Subcontracted by Evergreen to Huffman Laboratories of Golden, Colorado.

holding times is presented in Table 4.2 of the project Quality Assurance Project Plan (QAPP) (Parsons ES, 1994).

Waste soils generated during soil sampling operations were spread on the ground surface in the vicinity of the site. The near-surface portions of soil boreholes that didn't collapse following removal of the Geoprobe® rods were backfilled with native soils.

One sediment sample (24SS-2, Figure 2.2) was collected from the top 3 inches of soil in a shallow drainage swale downstream of the contamination source area. Some soil discoloration had been noted at this location. The sample was collected using a stainless steel trowel, and was handled as described above for soil samples.

2.1.3 Monitoring Point Installation

Twenty-five groundwater monitoring points were installed at 15 locations under this program. Detailed monitoring point installation procedures are described in the work plan (Parsons ES, 1995a) and summarized in following paragraphs. Monitoring point completion diagrams are included in Appendix B.

2.1.3.1 Monitoring Point Materials Decontamination

Monitoring point completion materials were inspected by the field hydrogeologist and determined to be clean and acceptable prior to use. All monitoring point completion materials were factory sealed in plastic wrap. Pre-packaged casing, sand, bentonite, and concrete mix were used in point construction, and the bags were inspected for possible external contamination before use. Materials that could not be cleaned to the satisfaction of the field hydrogeologist were not used.

2.1.3.2 Monitoring Point Casing and Screen

Shallow monitoring points were installed in the 2-inch-diameter Geoprobe® boreholes. Each shallow point was constructed of Schedule 40 polyvinyl chloride (PVC) riser pipe and screen having an ID of 0.5-inch. All casing and screen sections were flush threaded; glued joints were not used. The riser pipe at each monitoring point was fitted with a PVC top cap, and a threaded PVC bottom cap was placed on the bottom of the screen. Monitoring point screens were 5 feet long and were factory slotted with 0.010-inch openings. Each shallow point was screened so that seasonal fluctuations of the water table could be measured and mobile LNAPL, if present on the groundwater surface, could be detected.

Deep monitoring points were installed through Geoprobe® drive rods having an outside diameter (OD) of 1 inch. Each deep point was constructed using 0.25-inch-ID, Teflon® or Teflon®-lined polyethylene tubing threaded through the center of the Geoprobe® drive rods and attached to a 0.5-foot-long, 0.375-inch-diameter stainless steel double-woven wire screen with a 0.037-inch mesh. The well screen was threaded into a dedicated stainless steel drive point/implant anchor that remained in place after the drive rods were removed. The tubing was fitted with a plastic top cap to prevent the entrance of water or sediment.

Manually driven shallow monitoring points each consisted of a 3-foot-long, 60-mesh (equivalent to slot size of 0.01 inch) stainless steel screen connected to galvanized steel riser pipe. A 6-inch-long galvanized iron drive point was attached to the base of the screen. The IDs and ODs of the screen and riser pipe were 1.38 inches and 1.66 inches, respectively. Manually driven deep monitoring points consisted of a 1-foot-long, 100-mesh (equivalent to an opening size of 0.006 inch) stainless steel screen connected to galvanized steel riser pipe. A stainless steel drive point was attached to the base of the screen. The IDs and ODs of the screen and riser pipe were 0.75 inch and 1.05 inches, respectively. The OD of the drive point and couplings was 1.25 inches.

The field hydrogeologist verified and recorded the borehole depth, the lengths of all casing sections and tubing, and the depth to the top of all monitoring point completion materials placed in the annulus between the casing/tubing and borehole wall. All lengths and depths were measured to the nearest 0.1 foot.

2.1.3.3 Sand Filter Pack

An attempt was made to place a graded 6-20 or 20-30 sand filter pack around the screened intervals of Geoprobe®-installed monitoring points. The washed and bagged sand was distributed by Standard Sand and Silica Company. However, placement of the filter pack around the monitoring point screens was usually compromised by the collapse of the sand borehole walls in the saturated zone. Therefore, most of the monitoring points are at least partially sand-packed with the native formation materials. However, due to the sandy nature of the formation materials, monitoring point development and purging activities were accomplished without incident. Sand filter packs were not installed around the screens of manually-driven monitoring points.

2.1.3.4 Annular Sealant

A filter pack seal of sodium bentonite pellets was placed above the sand pack (natural or introduced) in the Geoprobe® monitoring points. The filter pack seal was generally placed above the water table due to the collapse of saturated formation sands into the borehole following removal of the Geoprobe rods, and was hydrated in place with potable water. The thickness of the seal varied depending on the length of borehole remaining open following removal of the Geoprobe rods, but generally ranged from 0.5 to 2 feet. Bentonite seals were not installed in manually driven monitoring points.

2.1.3.5 Flush-Mount Protective Cover

Most monitoring points were completed with an 8-inch by 7.5-inch at-grade protective cover with a bolted cap. At these locations, the at-grade covers were cemented in place using concrete, and were completed with concrete pads that slope gently away from the protective covers to facilitate runoff during precipitation events. The space inside the protective covers (below the top of the riser pipe or tubing) was filled with native sandy soils to allow drainage of any precipitation that might collect within the cover. Monitoring points 24PZ-1S/1D, which are located within a densely forested area (Figure 2.2), were completed as projecting points, and were fitted with a slip cap.

2.1.4 Monitoring Point Development

Prior to sampling, newly installed monitoring points were developed. Typically, well development removes sediment from inside the well casing and flushes fines, cuttings, and drilling fluids from the sand pack and the portion of the formation adjacent to the well screen. Use of the Geoprobe® system to place monitoring points eliminates cuttings and drilling fluids. As a result, development of monitoring points was primarily intended to minimize the amount of fine sediment that might accumulate in the casing.

Monitoring point development was accomplished using a peristaltic pump with dedicated silicon and high-density polyethylene (HDPE) tubing. The pump tubing was regularly lowered to the bottom of the shallow points so that fines were agitated and removed from the point in the development water. Development was continued until 10 casing volumes of water were removed, and the pH, temperature, and conductivity of the groundwater had stabilized. All development waters from points in known or suspected areas of contamination were collected in 55-gallon steel drums and transferred to an oil/water separator located on the Base.

2.2 GROUNDWATER SAMPLING

This section describes the procedures used for collecting groundwater quality samples. In order to maintain a high degree of quality control (QC) during this sampling event, the procedures described in the site work plan (Parsons ES, 1995a) and summarized in the following sections were followed.

Groundwater sampling occurred in March 1995, and consisted of collecting groundwater samples from new monitoring points and existing monitoring wells. The five manually-driven monitoring points installed in July 1995 also were sampled in July, and monitoring point 24PZ-1S was resampled for aromatic VOCs at this time. In addition to the sampling events conducted under this program, CH2M Hill (1990 and 1991a) and Enserch Environmental (1994a and 1994b) have conducted groundwater sampling at the site.

2.2.1 Groundwater Sampling Locations

Groundwater samples were collected from all existing wells and newly installed monitoring points by Parsons ES personnel. Twenty-five new monitoring points, including 10 nested pairs (Table 2.1), were installed at the 15 locations shown on Figure 2.2. After completion of installation and development activities, the monitoring points and wells were purged and sampled using a peristaltic pump with dedicated HDPE and silicon tubing. The twelve existing monitoring wells installed by CH2M Hill (1990, 1991a) that were sampled under this program included MD24-1 through MD24-10, MD24-6A, and MD24-10A (Table 2.1 and Figure 2.2).

2.2.2 Preparation and Equipment Cleaning

All equipment used for sampling was assembled and properly cleaned and calibrated (if required) prior to use in the field. All portions of sampling and test equipment that contacted the sample were thoroughly cleaned before use. This equipment included the

water level probe and cable, equipment for measuring on-site groundwater chemical parameters, and other equipment that contacted the samples. The following cleaning protocol was used:

- Cleaned with potable water and phosphate-free laboratory-grade detergent;
- Rinsed with potable water;
- Rinsed with isopropyl alcohol;
- Rinsed with distilled or deionized water; and
- Air dried prior to use.

Any deviations from these procedures were documented in the field scientist's field notebook and on the groundwater sampling form.

As required, field analytical equipment was calibrated according to the manufacturers' specifications prior to field use. This requirement applied to direct reading meters used for on-site chemical measurements of DO, pH, redox potential, electrical conductivity, and temperature, as well as the Hach® meter used for other on-site geochemical analyses (Table 2.2).

2.2.3 Groundwater Sampling Procedures

Special care was taken to prevent contamination of the groundwater and extracted samples through cross contamination from improperly cleaned equipment. Water level probes and cable used to determine static water levels and total depths were thoroughly cleaned before and after field use and between uses at different sampling locations according to the procedures presented in Section 2.2.2. In addition, a clean pair of new, disposable latex gloves was worn each time a different well or point was sampled.

2.2.3.1 Preparation of Location

Prior to starting the sampling procedure, the area around the well/point was cleared of foreign materials, such as brush, rocks, and debris. These procedures prevented sampling equipment from inadvertently contacting debris around the monitoring well/point. The integrity of the monitoring well/point was also inspected, and any irregularities in the visible portions of the well or point, protective cover, or concrete pad were noted.

2.2.3.2 Water Level and Total Depth Measurements

Prior to removing any water from the well or shallow monitoring point, the static water level was measured. In the shallow, 0.5-inch-diameter PVC monitoring points, an electrical water level probe was used to measure the depth to groundwater below the well datum to the nearest 0.01 foot. An oil/water interface probe capable of measuring the depth to both petroleum product (if present) and water was used in the previously installed 2-inch-diameter wells. Water levels in the newly installed points constructed of Teflon® or Teflon®-lined HDPE tubing were not obtained because the diameter of

the water level probe was larger than the diameter of the tubing. After measurement of the static water level, the water level probe was lowered to the bottom of the well/point for measurement of total depth (recorded to the nearest 0.1 foot). Based on these measurements, the volume of water to be purged from the wells/points was estimated.

2.2.3.3 Monitoring Well/Point Purging

Where possible, purging was performed until three times the calculated casing volume was removed from each well or point prior to sampling, and until the pH, DO concentration, redox potential, conductivity, and temperature stabilized for a 1-minute period. A peristaltic pump with dedicated silicon and HDPE tubing was used for well/point evacuation. Purge water from areas believed to be contaminated based on field observations and historical groundwater quality data was disposed of in the designated Base oil/water separator. Water presumed to be clean based on field PID screening and historical data was discharged onto the ground surface in the vicinity of the sampling location.

2.2.3.4 Sample Collection

A peristaltic pump with dedicated silicon and HDPE tubing was used to extract groundwater samples from each well and monitoring point. Purging and sampling constituted one continuous sampling event, and there was no cessation of pumping prior to sample collection. For shallow monitoring points, the dedicated HDPE tubing was lowered down the casing to approximately the middle of the screened interval. Sampling from the deep points, constructed of tubing, was accomplished by attaching the silicon tubing directly to the top of the monitoring point tubing using a hose barb. Samples for laboratory analysis were transferred directly into the appropriate sample containers. The water was carefully poured down the inner walls of each sample bottle to minimize aeration of the sample. Sample bottles for aromatic VOCs, TVH, methane, anions, alkalinity, halogenated VOCs, and Hach® field analyses were filled so that no headspace or air bubbles remained within the container. Table 2.2 lists the analyses performed on collected groundwater samples.

2.2.4 Onsite Chemical Parameter Measurement

2.2.4.1 Dissolved Oxygen Measurements

DO measurements were taken using an Orion® model 840 DO meter in a flow-through cell at the outlet of the peristaltic pump. DO concentrations were recorded after the readings stabilized, and in all cases represent the lowest DO concentration observed. The DO meter was periodically checked against both a zero-oxygen solution and a solution of oxygenated tap water. The meter provides readings to the nearest 0.01 mg/L, but in reality, measurement to this level of precision is probably not meaningful.

2.2.4.2 Electrical Conductivity, pH, Redox Potential, and Temperature Measurements

The electrical conductivity, pH, redox potential, and temperature of the groundwater were measured in the field, in the same flow-through cell used for DO measurements. The measured values were recorded on the groundwater sampling record (Appendix B).

2.2.4.3 Hach® and CHEMetrics® Field Chemistry Measurements

An onsite laboratory staffed by Parsons ES personnel was used to analyze for several indicator parameters in groundwater samples collected from existing monitoring wells and newly installed monitoring points. A Hach® DR/700 colorimeter was used to measure ferrous iron (Fe^{2+}), total iron (Fe), nitrate (NO_3^-), nitrite (NO_2^-), sulfate (SO_4^{2-}), manganese (Mn^{2+}), and sulfide (S^{2-}). Titrations using Hach® reagents were conducted to measure alkalinity [as milligrams per liter (mg/L) calcium carbonate (CaCO_3)] and chloride (Cl^-). CHEMetrics® color tests were used to measure ammonia (NH_3) and carbon dioxide (CO_2). These analyses were completed for each groundwater sample after all sample containers had been filled. The sample to be analyzed was poured into a clean glass container, capped, and transported to the Parsons ES on-Base laboratory for analysis. Care was taken to avoid any headspace in the sample container, which could influence the concentration of reduced species. The field holding time for each sample did not exceed 1 hour. Care was taken to minimize sample temperature changes and exposure to sunlight. Concentrations of these indicator parameters were not measured in soil samples.

2.2.5 Sample Handling

2.2.5.1 Sample Containers, Preservation, and Labels

The off-Base analytical laboratories (EAL and USEPA's NRMRL) provided pre-preserved sample containers when appropriate. NRMRL provided a separate preservative for methane analysis, which was added to the samples by the Parsons ES field personnel.

The sample containers were filled as described in Section 2.2.3.4, and the container lids were tightly closed. The sample label was firmly attached to the container side, and the following information was legibly and indelibly written on the label:

- Analysis to be performed;
- Facility name;
- Sample identification;
- Sample type (groundwater);
- Sampling date;
- Sampling time;
- Preservatives added; and

- Sample collector's initials.

2.2.5.2 Sample Shipment

After the samples were sealed and labeled, they were packaged for transport to EAL in Wheat Ridge, Colorado or to NRMRL in Ada, Oklahoma. The following packaging and labeling procedures were followed:

- Samples were packaged to prevent leakage or vaporization from the containers;
- Samples were cushioned to avoid breakage; and
- Ice was added to the cooler to keep the samples cool.

The packaged samples were delivered by overnight courier (Federal Express®) to the laboratories. Chain-of-custody procedures outlined in the project work plan (Parsons ES, 1995a) were followed. Laboratory samples for field analysis were hand-delivered to the on-Base Parsons ES laboratory, where they were analyzed by Parsons ES using methods and reagents developed and sold by Hach Chemical Company and CHEMetrics.

2.3 AQUIFER TESTING

Slug tests were performed in wells MD24-10A and MD24-4 (Figure 2.2) for comparison to the previous hydraulic conductivity estimates obtained by CH2M Hill (1990). Slug tests are single-well hydraulic tests used to estimate the hydraulic conductivity of an aquifer in the immediate vicinity of the tested well. Slug testing can be performed using either a rising head or a falling head test. Both rising head and falling head tests were used at this site. Detailed slug testing procedures are presented in the *Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater* (Wiedemeier *et al.*, 1995b), hereafter referred to as the Technical Protocol document.

Data obtained during slug testing were analyzed using the computer program AQTESOLV® (Geraghty & Miller, Inc. 1994) and the methods of Bouwer and Rice (1976) and Bouwer (1989) for unconfined conditions. The results of slug testing are presented in Section 3.5 and Appendix B.

2.4 SURVEYING

After completion of field work, the locations and elevations of all new monitoring points and pre-existing monitoring wells were surveyed by Landmark Surveying and Engineering, Inc. of Tampa, Florida. The horizontal locations and elevations of the measurement datum (top of PVC well casing) and the ground surface adjacent to the well casing were measured relative to existing on-Base survey control points. Horizontal locations were surveyed to the nearest 0.1 foot. Measurement datum and ground surface elevations were surveyed to the nearest 0.01 foot relative to mean sea level (msl). Survey data are contained in Table 2.1 and Appendix B.

SECTION 3

PHYSICAL CHARACTERISTICS OF THE STUDY AREA

This section incorporates data collected by Parsons ES in March through October 1995 and data collected by CH2M Hill (1990, 1991a, and 1991b), Enserch Environmental (1994a and 1994b), and Black & Veatch Waste Science, Inc. (BVWS, 1995). The BVWS report is for another site at MacDill AFB.

3.1 VEGETATION CHARACTERISTICS, GROUND SURFACE TOPOGRAPHY AND SURFACE WATER HYDROLOGY

The Base is located on the western edge of Central Florida in the Southeast Coastal Plain Physiographic Province, a region characterized by slight local relief and low elevations. A topographic map of the Base area is presented in Figure 1.2. Elevations at the Base range from 0 to 12 feet above msl. Major surface water bodies near the Base include Tampa Bay, which borders the Base on the west and south; Hillsborough Bay, which forms the eastern border of the Base; and the Gulf of Mexico, which lies approximately 19 miles to the west (Figure 1.1). Three tidal inlets are present in mangrove swamps on the south side of the Base, including Coon Hammock Creek, Picnic Island Creek, and Broad Creek (Figure 1.2). Other surface water features include storm drains and drainage canals that traverse the Base, and small ponds, lakes, and mangrove swamps. Surface water runoff is controlled by the drainage canals and swamps, which discharge into Tampa Bay and Hillsborough Bay.

The ground surface in the vicinity of Site OT 24 is relatively flat, with elevations ranging from approximately 3 to 6 feet msl. As shown on Figure 1.2, the nearest surface drainage feature is a canal located at the Base property boundary approximately 350 feet north of the EMTL. Groundwater elevation measurements indicate that this canal is hydraulically upgradient from the site, and therefore it does not represent a potential discharge area for site-related contamination dissolved in the groundwater. The nearest downgradient drainage canal is located approximately 900 feet south of the EMTL. Water in this canal, which is approximately 30 feet wide directly south of the EMTL, eventually discharges into Tampa Bay, approximately 5,000 feet southwest of the site. A topographically low, swampy area populated by mangroves borders the canal on its northern side. This mangrove swamp extends to the north for approximately 150 feet, to within 750 feet of the EMTL (Figure 2.2). Shallow (less than or equal to 2-foot-deep) drainage swales are located immediately south and southwest of the EMTL (Figure 1.3). During and immediately following precipitation events, water ponds in these areas, and during very wet periods when the water table is near the ground surface, some groundwater discharge may occur. However, these swales do not appear to receive significant volumes of groundwater discharge.

A densely forested area is present south and southeast of the EMTL, as shown on Figure 2.2. The dominant plant species in the area south of the EMTL is Brazilian pepper. A few cabbage palms, salt bush, smooth cordgrass, and occasional mangroves are also present within the dense growth of Brazilian pepper, depending on the ground surface elevation. The plants in this portion of the forested area are probably relatively efficient at evapotranspiring groundwater to the atmosphere. A narrow band of laurel oak separates the higher, pepper-dominated area from the lower-elevation mangrove swamp described above.

3.2 CLIMATE

According to BVWS (1995), the average annual precipitation at the Base is 44.3 inches, with the lowest rainfall in April and the highest in August. The reported average annual evapotranspiration (ET) is 39 inches. However, ET rates will vary depending on the vegetative cover. ET rates for the densely forested area south of Site OT24 are probably higher than for the surrounding grass-covered areas.

3.3 MANMADE FEATURES

The locations and functions of pertinent current and former manmade features such as the EMTL and the former drain fields are described in Section 1.2. As shown on Figure 1.3, much of the land surface surrounding the site is unpaved. A substantial percentage of the precipitation falling on unpaved areas probably infiltrates into the subsurface due to the flat surface topography and sandy soils. The extent to which underground utility corridors influence groundwater movement is not known. However, significant preferential movement of contaminants along utility corridors was not indicated by the previous site characterizations (CH2M Hill, 1990 and 1991a). The relatively sandy nature of the soils in the saturated zone, and the resulting higher permeabilities, would tend to minimize preferential migration of contaminants along utility corridors relative to surrounding areas.

3.4 REGIONAL GEOLOGY AND HYDROGEOLOGY

The information provided in this section is condensed from more detailed discussions presented by BVWS (1995) and CH2M Hill (1990 and 1991a). The unconsolidated, Quaternary-age, coastal plain sediments found at the surface in the Tampa area consist predominantly of fine sand containing interbedded clay, marl, shell, limestone, and phosphorite. These sediments, which form the surficial, unconfined aquifer, range in thickness from almost zero to approximately 100 feet. The water table depth ranges from the ground surface to several feet below the ground surface.

The surficial aquifer is underlain by Pliocene-age deposits consisting of phosphatic, clayey and pebbly sand, clay, marl, and shell. These deposits, which range from less than 25 feet to about 100 feet in thickness and comprise a confining layer, are underlain by carbonate and clastic sediments of the Hawthorn Formation and Tampa Limestone. The solutioned Tampa Limestone forms the uppermost confined limestone aquifer. The limestones of the Florida Aquifer, which provide water for most of Florida and the southern third of Georgia, lie beneath the Tampa Limestone aquifer.

At the Base, the surficial, unconfined aquifer consists of 20- to 60-foot-thick layers of fine quartz sand, silty sand, and clayey sand that overlie a clay unit. The Tampa Limestone occurs beneath the clay and is estimated to be approximately 100 feet thick. In some areas, the surficial and Tampa Limestone aquifers may be hydraulically connected.

3.5 SITE GEOLOGY AND HYDROGEOLOGY

The locations of two site-specific hydrogeologic cross-sections are depicted in Figure 3.1, and the sections are shown in Figures 3.2 and 3.3. The groundwater surface beneath the vicinity of the EMTL was present at a depth of 2.2 to 5.3 feet bgs in March 1995 (Table 3.1). Historical groundwater elevation data collected from April 1989 to October 1995 suggest that water levels may fluctuate by as much as 4 feet between wet and dry periods.

Sediments underlying the site that comprise the surficial aquifer consist primarily of fine- to medium-grained sand containing up to 12 percent silt and clay. Isolated zones of silty sand, containing greater than 12 percent silt/clay, were encountered at some locations. The surficial aquifer is underlain by clay and limestone. The clay, which may represent a weathering horizon on top of the limestone, was encountered at a depth of 56 feet in borehole MD24-9, 25 feet in borehole MD24-7, 29 feet in borehole MD24-10, 26 feet in borehole MD24-MW6A, and 10.5 feet bgs in borehole 24MP-6. Borehole 24MP-6 is located approximately 400 feet northeast of the EMTL (Figure 3.1). Silty, clayey sand was encountered at a depth of approximately 25 feet in borehole MD24-3. These data suggest that the thickness of the surficial aquifer in the vicinity of the EMTL ranges from less than 10 feet to approximately 53 feet, using an average groundwater depth of 3 feet bgs. The average depth to the clay zone in the three boreholes that are most directly downgradient from the contamination source(s) (MD24-6, MD24-7, and MD24-10) is 27 feet bgs. Therefore, the average thickness of the surficial aquifer along the flowpath of the dissolved BTEX plume is estimated to be approximately 24 feet. This value is similar to the aquifer thickness of 20 feet assumed by CH2M Hill (1991b) for design of the groundwater and product recovery systems at the EMTL.

Groundwater elevations measured by Parsons ES in March 1995, August 1995, and October 1995 are shown on Figures 3.4, 3.5, and 3.6, respectively. The groundwater elevation isopleths indicate a southwesterly groundwater flow direction in the immediate vicinity of the EMTL, which is consistent with the data for August 1989 presented by CH2M Hill (1991a) (Appendix A). As shown on Figures 3.5 and 3.6, further downgradient from the site the groundwater flow direction shifts toward the south-southeast. This apparent shift in the dominant flow direction may be caused by variations in ET rates across the study area. The ET rates in the densely forested area south of the site are probably high relative to those in the surrounding area due to the abundance of plants with roots that extend into the saturated zone. The higher ET rates may cause the groundwater surface beneath the forested area to be depressed relative to surrounding, less vegetated areas, which could result in a bending of the groundwater flow lines toward this area. The lateral hydraulic gradients measured in August 1989, March 1995, August 1995, and October 1995 ranged from 0.0016 foot per foot (ft/ft) to 0.0048 ft/ft, and averaged 0.0030 ft/ft. According to CH2M Hill (1990), drain field

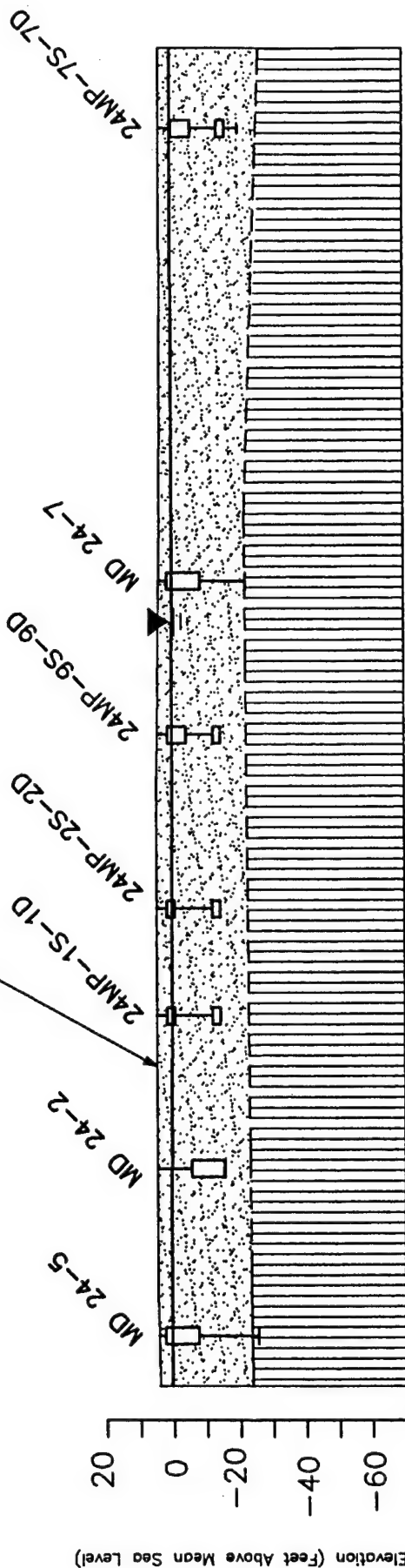
NE

SW

A

A'

FORMER DRAIN FIELD



MD 24-2
Monitoring Well/Point
Identification

Brown to light-gray, poorly to well-sorted,
fine-to medium-grained SAND.



Moist, highly plastic CLAY and LIMESTONE.



Borehole
Screened Interval
Bottom of Borehole

Location of Water Table
on March 24, 1995

Stratigraphic Contact
(Dashed where inferred)

0 25 50 100
Horiz. and Vert. Scales: 1"=50'

FIGURE 3.2

HYDROGEOLOGIC CROSS-SECTION A-A'

Site OT 24

Intrinsic Remediation TS

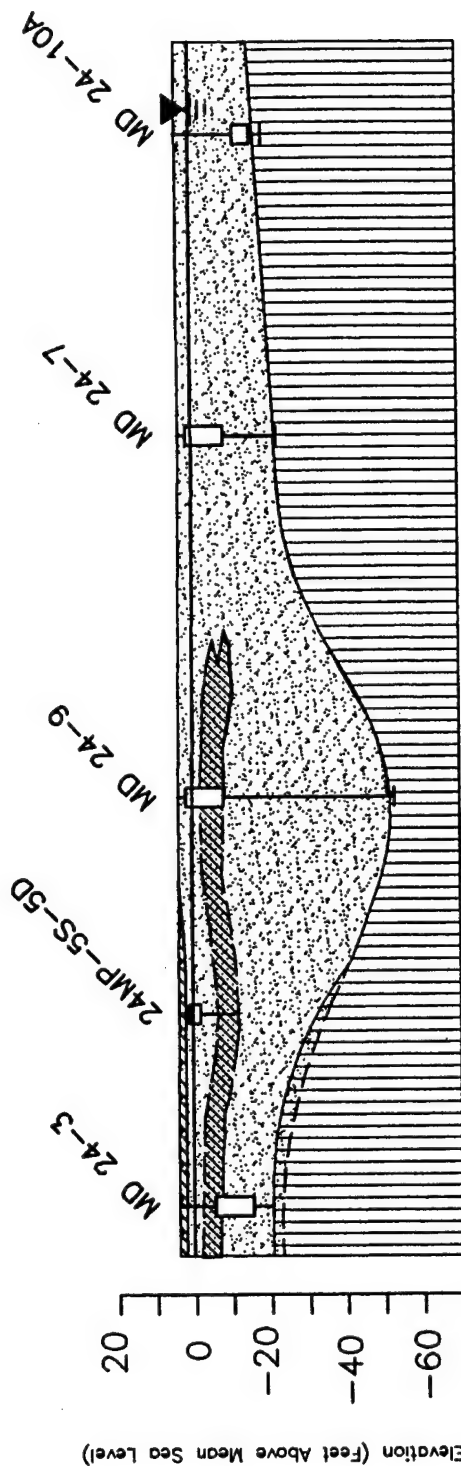
MacDill Air Force Base, Florida

**PARSONS
ENGINEERING SCIENCE, INC.**

Denver, Colorado

S
B

N
B



0 25 50 100
Horiz. and Vert. Scales: 1"=50'

FIGURE 3.3

HYDROGEOLOGIC CROSS-SECTION B-B'

Site OT 24
Intrinsic Remediation TS
MacDill Air Force Base, Florida

**PARSONS
ENGINEERING SCIENCE, INC.**

Denver, Colorado

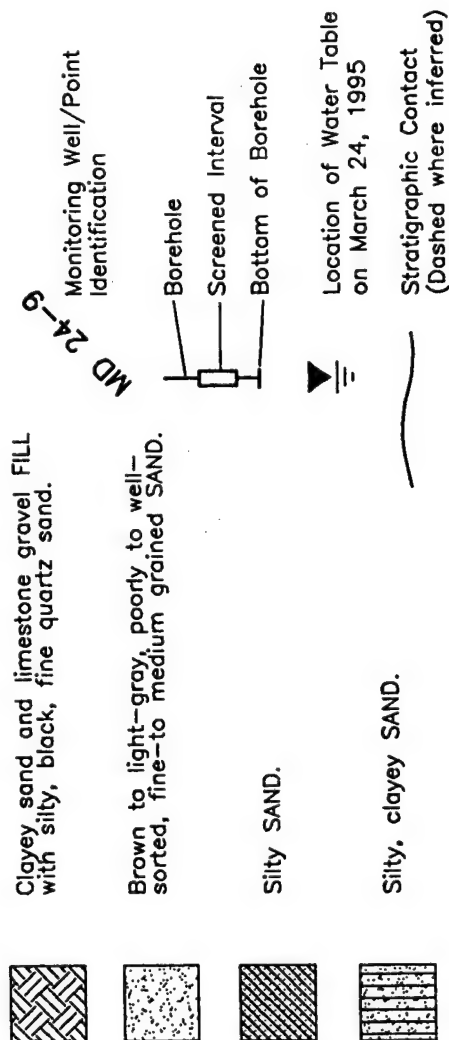


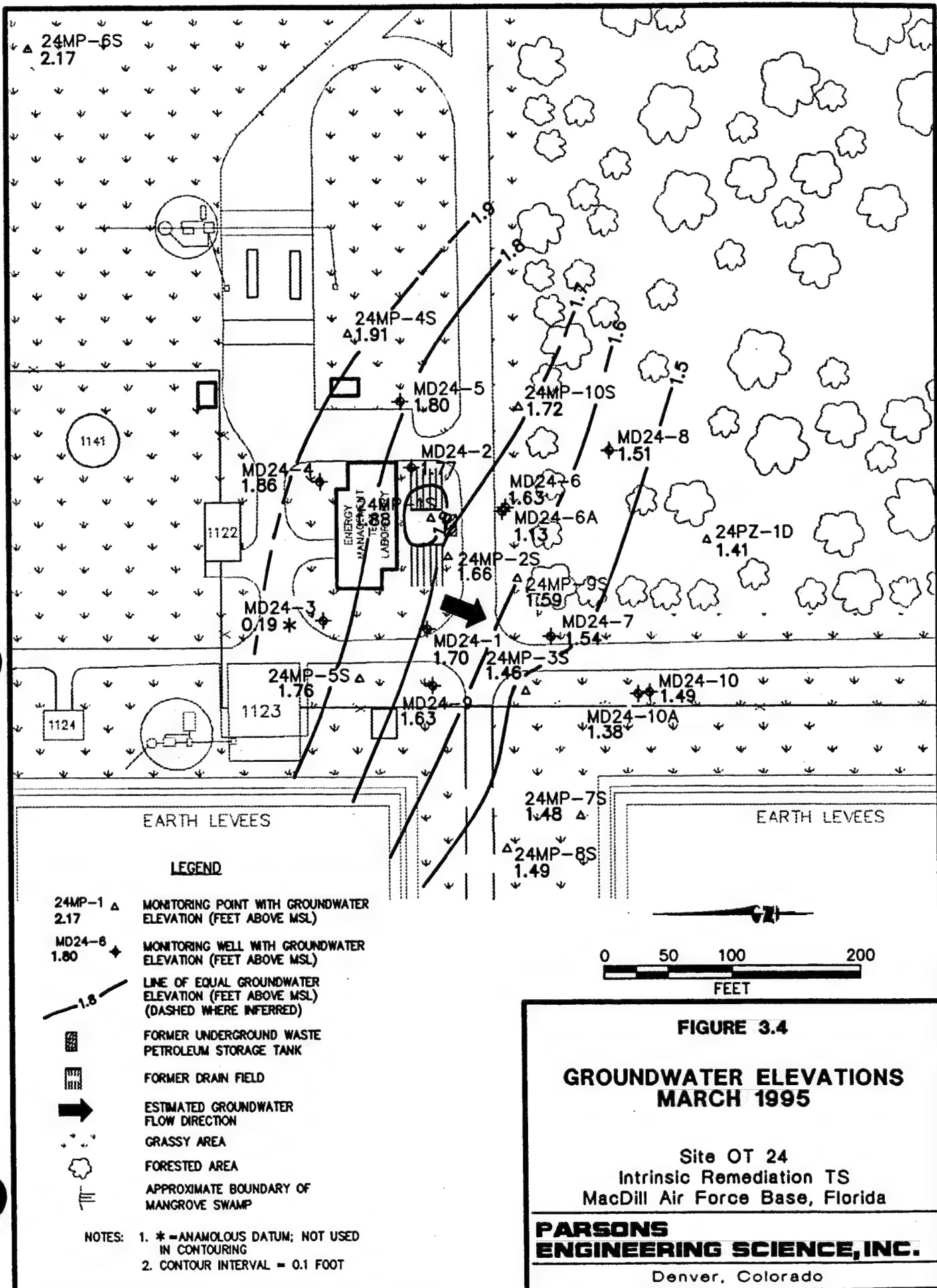
TABLE 3.1
WATER LEVEL DATA
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Well Location	Datum Elevation (ft msl) ^u	Total Depth to Water 3/24/95 (ft btoc) ^v	Elevation of Water Table 3/24/95 (ft msl)	Total Depth to Water 8/11/95 (ft btoc)	Elevation of Water Table 8/11/95 (ft msl)	Total Depth to Water 10/10/95 (ft btoc)	Elevation of Water Table 10/10/95 (ft msl)
24MP-1S	5.58	3.70	1.88	NM ^w	NM	1.69	3.89
24MP-2S	4.94	3.28	1.66	NM	NM	0.65	4.29
24MP-3S	4.00	2.54	1.46	NM	NM	NM	NM
24MP-4S	5.38	3.47	1.91	NM	NM	0.55	4.83
24MP-5S	5.19	3.43	1.76	NM	NM	0.88	4.31
24MP-6S	4.50	2.33	2.17	NM	NM	NM	NM
24MP-7S	4.00	2.52	1.48	NM	NM	0.44	3.56
24MP-8S	4.15	2.66	1.49	NM	NM	NM	NM
24MP-9S	3.60	2.01	1.59	NM	NM	NM	NM
24MP-10S	4.20	2.48	1.72	NM	NM	NM	NM
MD 24-1	8.88	7.18	1.70	NM	NM	4.65	4.23
MD 24-2	8.03	6.26	1.77	NM	NM	3.54	4.49
MD 24-3	8.23	8.42	-0.19	NM	NM	3.81	4.42
MD 24-4	8.51	6.65	1.86	NM	NM	3.94	4.57
MD 24-5	4.89	3.09	1.80	NM	NM	0.13	4.76
MD 24-6	4.40	2.77	1.63	1.02	3.38	0.17	4.23
MD 24-6A	4.70	3.07	1.63	1.31	3.39	0.48	4.22
MD 24-7	4.13	2.59	1.54	1.13	3.00	0.21	3.92
MD 24-8	4.36	2.85	1.51	NM	NM	NM	NM
MD 24-9	4.53	2.90	1.63	1.5	3.03	0.42	4.11
MD24-10	3.71	2.22	1.49	NM	NM	0.03	3.68
MD 24-10A	3.66	2.28	1.38	NM	NM	-0.01	3.67
24PZ-1S	6.32	4.90	1.42	3.55	2.77	3.09	3.23
24PZ-1D	5.54	4.13	1.41	NM	NM	NM	NM
24PZ-2S	4.16	1.65	2.51	1.65	2.51	0.76	3.40
24PZ-3S	3.75	1.45	2.30	1.45	2.30	0.48	3.27
24PZ-3D	3.82	NM	NM	NM	NM	NM	NM
24PZ-4S	4.43	1.82	2.61	1.82	2.61	NM	NM
24PZ-5S	4.40	2.29	2.11	2.29	2.11	1.16	3.24

^u ft msl = feet relative to mean sea level.

^v ft btoc = feet below top of casing.

^w NM = not measured.



discharge did not appear to have a significant impact, if any, on groundwater levels during their investigation.

Comparison of groundwater elevations in two nested well pairs (MD24-6/6A and MD24-10/10A) indicates that in March 1995, a vertical (downward) component to the hydraulic gradient was present at MD24-10/10A. Using the head difference between the shallow and deep wells, and the distance between the midpoints of the saturated portions of their screens, the magnitude of the downward vertical hydraulic gradient at this well pair was calculated to be 0.006 ft/ft. The groundwater elevations in MD24-6 and -6A were equal, indicating that no vertical gradients were present. In October 1995, a slight downward gradient of 0.0005 ft/ft was measured at well pair MD24-10/10A, and a slight downward gradient of 0.0007 ft/ft was measured at well pair MD24-6/6A.

A total of nine slug tests were performed by CH2M Hill (1990) in Site OT 24 monitoring wells screened in the surficial aquifer. The resulting hydraulic conductivity (K) values ranged from 5 to 17 feet per day (ft/day) [1.8×10^{-3} to 6.0×10^{-3} centimeters per second (cm/sec)] and averaged 9 ft/day (3.2×10^{-3} cm/sec). The slug tests performed by Parsons ES yielded hydraulic conductivity values of 6.9 ft/day (2.4×10^{-3} cm/sec) at well MD24-10A and 14.1 ft/day (5.0×10^{-3} cm/sec) at MD24-4. Eleven hydraulic conductivity values derived from Hydrocone® testing at depths of 7 to 18 feet bgs ranged from 0.6 to 57 ft/day (2.1×10^{-4} to 2.0×10^{-2} cm/sec) and averaged 8.1 ft/day (2.9×10^{-3} cm/sec).

In addition, CH2M Hill (1990) performed a 48-hour aquifer pumping test immediately adjacent to the EMTL. Transmissivity values derived from analysis of drawdowns in observation wells ranged from 98 to 223 square feet per day (ft²/day). Assuming an average aquifer thickness of 20 feet, the hydraulic conductivity of the tested portion of the surficial aquifer would range from 5 to 11 ft/day. CH2M Hill (1991b) considered a transmissivity value of 223 ft²/day to be representative of the surficial aquifer for the portion of the aquifer tested.

The advective velocity of groundwater in the direction parallel to groundwater flow is given by:

$$\bar{v} = \frac{K}{n_e} \frac{dH}{dL}$$

Where: \bar{v} = Average advective groundwater velocity (seepage velocity) [L/T]

K = Hydraulic conductivity [L/T]

dH/dL = Gradient [L/L]

n_e = Effective porosity.

The average effective porosity of the surficial aquifer is estimated to be 0.25 based on literature values presented by Johnson (1967) and Walton (1988) for soils similar to those encountered at the site. Based on an average hydraulic conductivity of 9 ft/day, an average hydraulic gradient of 0.003 ft/ft, and an effective porosity of 0.25, the average advective groundwater velocity within the shallow, sandy aquifer is approximately 0.1 ft/day (36 ft/year).

Because organic carbon is generally present in the aquifer matrix, a somewhat retarded velocity (V_R) should be used for solute transport calculations. Section 4.2.3 presents TOC analysis results, and Section 5 contains V_R calculations.

3.6 GROUNDWATER USE

Groundwater from the shallow aquifer at MacDill AFB is not extracted for potable use, and there are no private wells located on the Base (BVWS, 1994). The nearest Hillsborough County designated Wellhead Protection Area is located approximately 13 miles north of the Base. Therefore, there are no public water supply wells within 0.5-mile of Site OT 24 [Southwest Florida Water Management District (SWFMD), 1988]. According to CH2M Hill (1990), no potable water wells are reported to be present within a 0.25-mile radius of the site. The closest potable well is approximately 0.25-mile north of the northern boundary of the Base (Engineering-Science, Inc., 1988). As shown on Figure 1.2, the EMTL is located approximately 350 feet (0.07 mile) south of the Base boundary. Therefore, the nearest potable water well is located approximately 0.32 mile north of (hydraulically upgradient from) the EMTL.

SECTION 4

NATURE AND EXTENT OF CONTAMINATION AND SOIL AND GROUNDWATER GEOCHEMISTRY

4.1 SOURCES OF CONTAMINATION

Original sources of contamination at Site OT 24 include infrastructure associated with the EMTL from which fuel was released into the subsurface. Mobile LNAPL, inferred to be present at the site, acts as a continuing source of groundwater contamination.

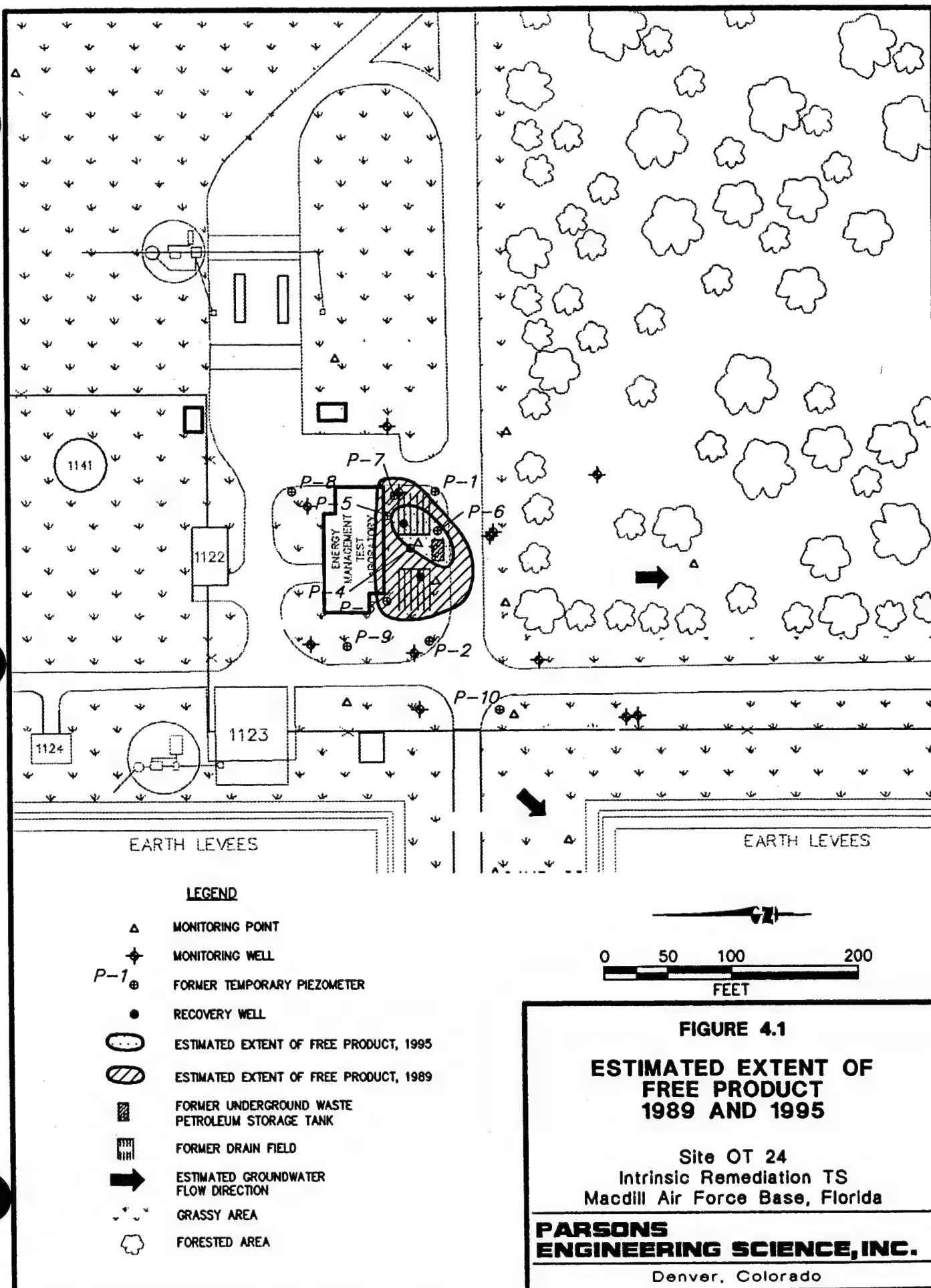
4.1.1 Source of Fuel Releases

Potential contamination sources at Site OT 24 include the former drain fields, former waste fuel UST, and former oil/water separator, all of which were located immediately south of the EMTL. The features associated with these former sources were removed in 1991. Since removal of these facilities, no fuel releases have been documented.

4.1.2 Extent of Free Product

Mobile LNAPL, inferred to be present at Site OT 24, constitutes a continuing source of contamination of groundwater. LNAPL thickness measurements were obtained by CH2M Hill (1990) in temporary piezometers P-1 through P-10 in September and October 1989. The estimated areal extent of mobile LNAPL during this period is shown on Figure 4.1, and LNAPL thickness measurements are presented in Appendix A. Measurable LNAPL thicknesses ranging from 0.57 foot to 3.12 feet were present in P-3 through P-7. It is well documented that LNAPL thickness measurements taken in groundwater monitoring wells are not indicative of actual mobile LNAPL thicknesses in the formation. According to Mercer and Cohen (1990), the measured LNAPL thickness in a well is typically 2 to 10 times greater than the actual mobile LNAPL thickness in the formation. CH2M Hill (1990) performed product bail-down tests to better determine the true product thickness within the formation. The bail-down tests indicated that actual product thicknesses ranged from 0.10 foot to 0.68 foot.

Investigative activities performed in 1995 indicated that mobile LNAPL was not completely removed by the soil excavation and product removal activities that occurred in 1991. In March 1995, an oil/water interface probe was used to check for the presence of LNAPL in all existing wells installed by CH2M Hill. Mobile LNAPL was detected only in what appeared to be a recovery well located at the former eastern drain field (Figure 4.1) at a thickness of 0.42 foot. A sample of this product was analyzed for aromatic VOCs at the USEPA NRMRL in Ada, Oklahoma. Analysis results for



this sample, and analysis results for a typical fresh JP-4 sample, are listed in Table 4.1. JP-4, which was formulated in the early 1950s, has remained the primary jet fuel for the US Air Force (Martel, 1987). Therefore, it is likely that weathered JP-4 is present at the site.

Comparison of the BTEX contents of the product sample obtained at Site OT 24 and fresh JP-4 indicates that the LNAPL present at the site is highly weathered. This is not surprising given the shallow depth to groundwater, warm temperatures, and high precipitation rate present at the Base.

In October 1995, during a water level measurement round, a strong petroleum odor was noted on the water level probe following a measurement in monitoring point 24MP-1S, and the water level in this monitoring point was depressed relative to surrounding wells, suggesting that LNAPL was present on the groundwater surface at this location. However, the presence of LNAPL could not be verified with an oil/water interface probe due to the small diameter of the monitoring point casing. A product measurement was not obtained in the adjacent recovery well. The data presented above indicate that the areal extent of mobile LNAPL is currently limited to the immediate vicinity of the former eastern drain field (Figure 4.1). As discussed in Section 4.3, residual LNAPL may also contribute to groundwater contamination.

4.2 SOIL CHEMISTRY

4.2.1 Soil and Sediment Headspace Screening

Soil and sediment headspace screening using an organic vapor analyzer (OVA) was performed by CH2M Hill (1990) in June 1989 to preliminarily delineate the lateral extent of petroleum contaminated soil at Site OT 24. A total of 34 samples were collected from 19 locations for screening purposes. Sample locations are shown on Figure 4.2, and quantitative screening results are contained in Appendix A. Samples at locations 1 through 7 consisted of sediment from the shallow drainage swale located south of the EMTL, collected from a depth of 0 to 1 foot bgs. Sample locations 8 through 19 were in the grassy areas immediately south, southeast, and southwest of the EMTL. At these locations, sample depths ranged from 0 to 3 feet bgs. The area of contaminated soil/sediment delineated on Figure 4.2 contained headspace readings greater than or equal to 100 parts per million, volume per volume (ppmv). Headspace sampling results ranged up to greater than 10,000 ppmv.

4.2.2 Magnitude and Extent of BTEX and Total Petroleum Hydrocarbons in Soil and Sediment

Four of the headspace screening samples (numbers 3, 8, 10, and 12, Figure 4.2) were analyzed at a laboratory for aromatic VOCs using USEPA Method 8020 and for total petroleum hydrocarbons (TPH) using USEPA Method 418.1 (see Appendix A for complete results). Laboratory results for BTEX are shown, along with the March 1995 soil sampling results, on Figure 4.3, and a complete summary of 1995 soil quality results is provided in Table 4.2.

TABLE 4.1
PETROLEUM PRODUCT ANALYSIS RESULTS
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Analyte	Concentration in Fresh JP-4 ^{a/} (mg/L) ^{c/}	Concentration in Product Sample From Recovery Well ^{b/} (mg/L)
Benzene	3,750	4.93
Toluene	9,975	ND ^{d/}
Ethylbenzene	2,775	2.45
Xylenes	17,400	18.01
1,3,5 Trimethylbenzene	3,150	243
1,2,4-Trimethylbenzene	7,575	540
1,2,3-Trimethylbenzene	-- ^{e/}	585
1,2,4,5-Tetramethylbenzene	--	698
1,2,3,5-Tetramethylbenzene	--	1,880
1,2,3,4-Tetramethylbenzene	5,625	1,400
Naphthalene	3,750	845
1-Methylnaphthalene	5,850	2,380
2-Methylnaphthalene	4,200	1,750

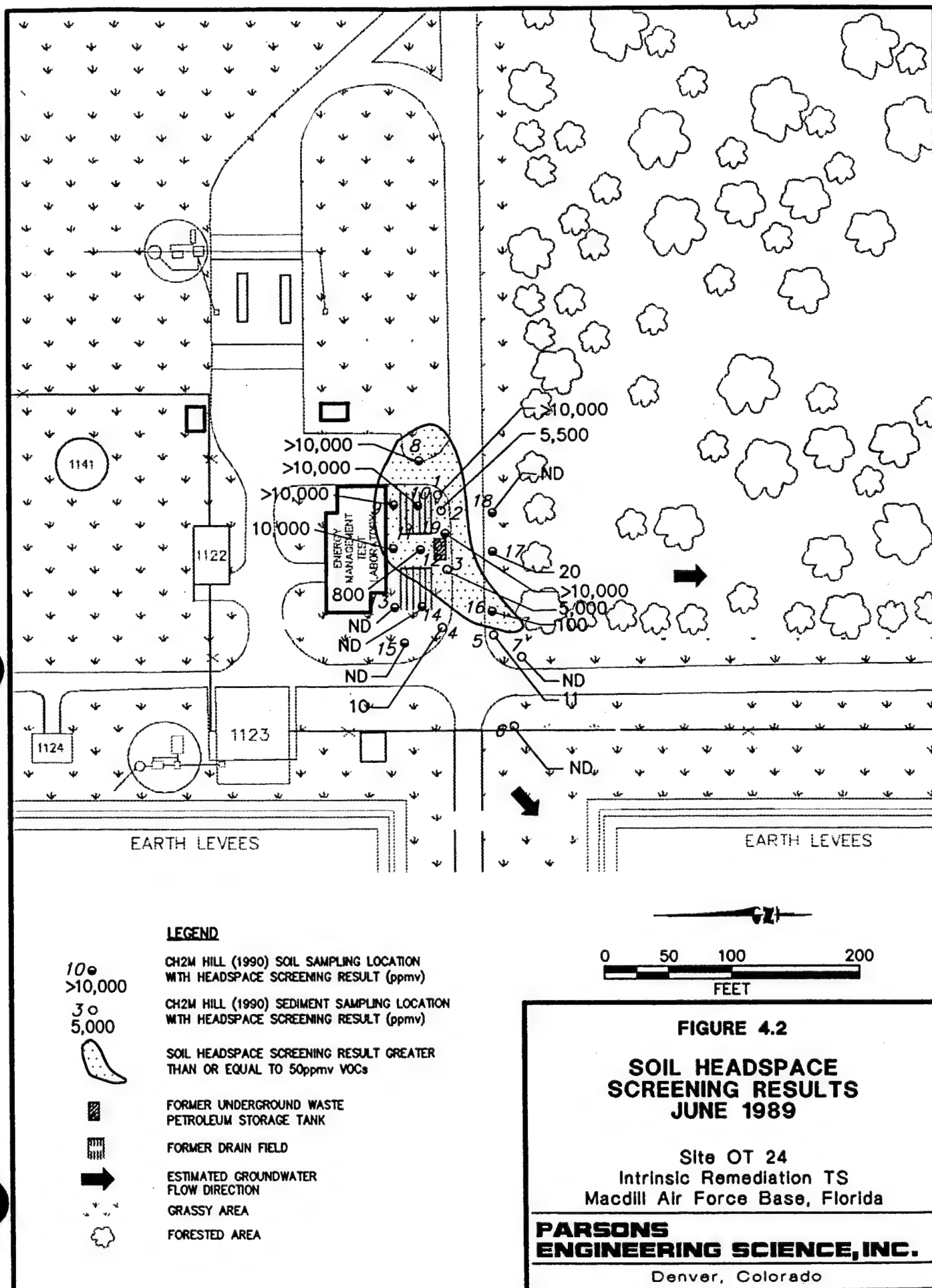
^{a/} Data from Arthur D. Little, Inc. (1987), corrected for the density of JP-4.

^{b/} Analyzed by USEPA NRMRL using a gas chromatograph/mass spectrometer (GC/MS) and a modification of method RSKSOP-124.

^{c/} mg/L = milligrams per liter.

^{d/} ND = not detected.

^{e/} Dash (--) = data not available.



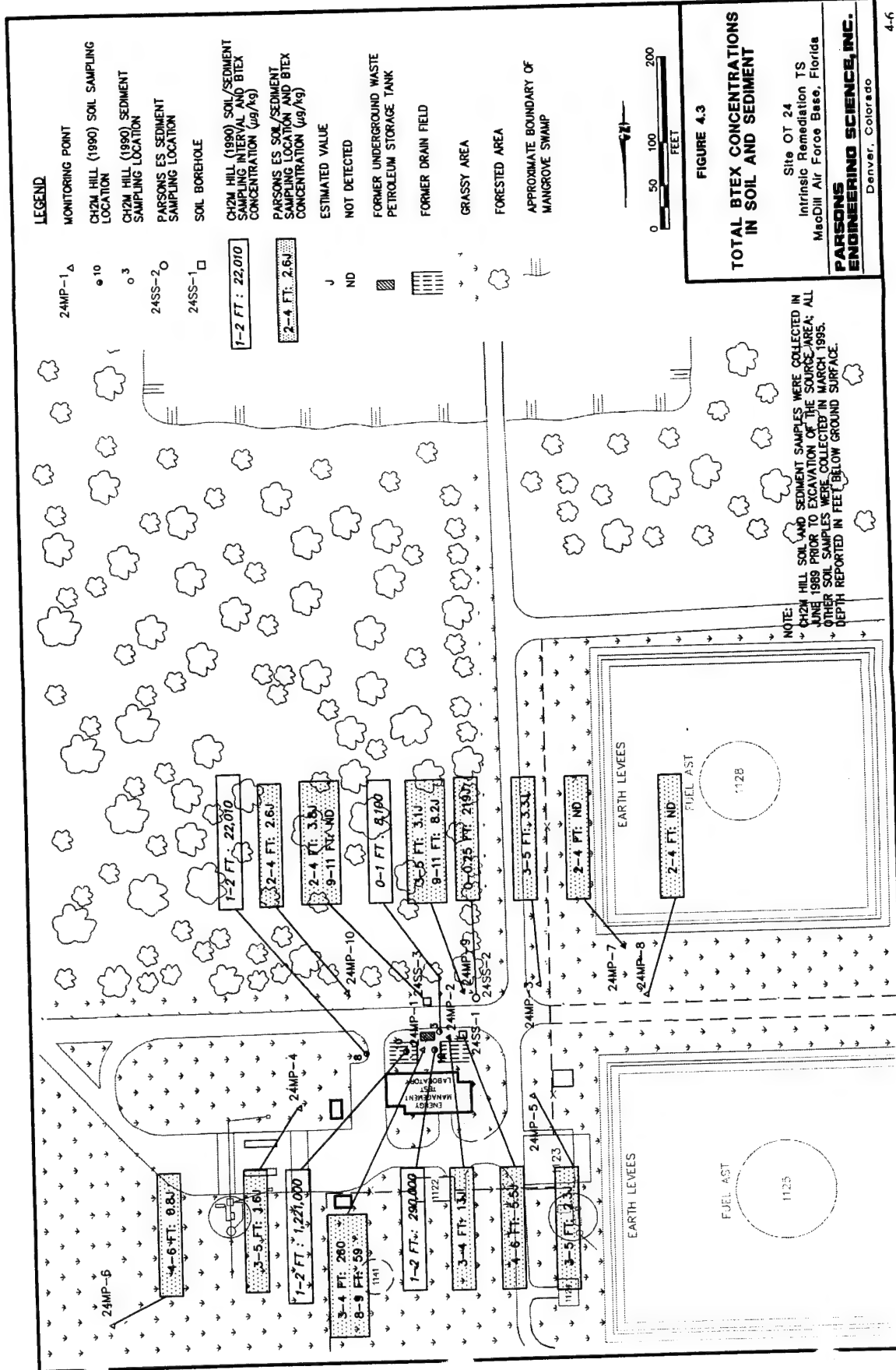


TABLE 4.2
1995 SOIL AND SEDIMENT DATA FOR FUEL RELATED COMPOUNDS
SITE OT 24

INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Sample Location	Sample Date	Sample Interval (feet)	Benzene (µg/kg) ^{g/}	Toluene (µg/kg)	Ethylbenzene (µg/kg)	Total Xylenes (µg/kg)	Total BTEX (µg/kg)	TEH ^{a/} (mg/kg) ^{b/}	TVH ^{b/} (mg/kg)	Chloro-benzene (µg/kg)	1,3,5-TMB ^{d/} (µg/kg)	1,2,4-TMB ^{d/} (µg/kg)	1,2,3-TMB ^{d/} (µg/kg)	1,2,3,4-TEMB ^{f/} (µg/kg)
24MP-1	3/8/95	3-4	14J ^{i/}	63	23	160	260	ND ^{j/}	ND	ND	37	59	40	20J
24MP-1	3/8/95	8-9	17	14	12	16	59	140	1.1	1.2J	5.9	6.4	3.4J	38
24MP-1C dup	3/8/95	8-9	12	12	11	16	51	NA ^{k/}	NA	1.4J	6.1	6.7	3.6J	37
24MP-2	3/8/95	3-4	ND	ND	ND	13J	13	11	ND	4.2J	9.5J	6.0J	ND	1.1J
24MP-3	3/9/95	3-5	ND	1.1J	ND	2.2J	3.3	ND	0.36	ND	ND	ND	ND	ND
24MP-4	3/9/95	3-5	ND	0.5J	ND	1.1J	1.6	ND	ND	ND	ND	ND	ND	ND
24MP-5	3/9/95	3-5	ND	2.3J	ND	ND	2.3	ND	ND	ND	ND	ND	ND	ND
24MP-6	3/9/95	4-6	ND	0.8J	ND	ND	0.8	ND	ND	ND	ND	ND	ND	ND
24MP-7	3/10/95	2-4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
24MP-8	3/10/95	2-4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
24MP-9	3/10/95	3-5	ND	2.5J	0.6J	ND	3.1	ND	0.17	ND	ND	ND	ND	1.1J
24MP-9	3/10/95	9-11	7.2	1.0J	ND	ND	8.2	ND	ND	ND	ND	ND	ND	1.1J
24MP-10	3/11/95	2-4	ND	ND	ND	2.4J	2.4	ND	ND	ND	ND	ND	ND	ND
24MP-10 dup	3/11/95	2-4	ND	ND	0.6J	2.2J	2.8	NA	NA	ND	ND	ND	ND	ND
24SS-1	3/10/95	4-6	ND	2.9J	ND	2.6J	5.5	210	4.7	ND	0.5J	ND	ND	42
24SS-2	3/10/95	4-6	ND	12J	37	170	219	32	3	27	150	140	200	850E ^{m/}
24SS-2 ^{i/}	3/23/95	0-0.25	ND	ND	ND	1.0J	1	64	ND	ND	2.0J	ND	ND	ND
24SS-3	3/11/95	2-4	ND	3.8J	ND	ND	3.8	ND	ND	ND	ND	ND	ND	3.2J
24SS-3	3/11/95	9-11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.0J

a/ TEH = total extractable hydrocarbons.

b/ TVH = total volatile hydrocarbons .

c/ 1,3,5-TMB = 1,3,5 trimethylbenzene.

d/ 1,2,4-TMB = 1,2,4 trimethylbenzene.

e/ 1,2,3-TMB = 1,2,3 trimethylbenzene.

f/ 1,2,3,4-TEMB = 1,2,3,4 tetramethylbenzene.

g/ µg/kg = micrograms

h/ mg/kg = milligrams p

i/ J = laboratory estimate.

j/ ND = not detected.

k/ NA = compound not analyzed for.

l/ Sediment sample.

m/ E = laboratory extrapolated value.

n/ TVH, and SW8020 for aromatic volatile

NOTE: Analysis methods included SW8015M for TEH and organic compounds, including TMB and TEMB compounds.

Samples collected in 1989 had BTEX and TPH concentrations ranging up to 1,221,000 micrograms per kilogram ($\mu\text{g/kg}$) [1,221 milligrams per kilogram (mg/kg)] and 22,580 mg/kg , respectively. The maximum detected BTEX and TPH concentrations occurred in the 1- to 2-foot sample from station 10. The distribution of detected concentrations suggests that the eastern drain field and/or the oil/water separator were major contaminant sources. The highest BTEX concentration detected in March 1995 was 260 $\mu\text{g/kg}$ at monitoring point 24MP-1. Detections of TVH in 1995 soil samples were all less than 5 mg/kg ; however, TEH concentrations in excess of 100 mg/kg were detected at monitoring point 24MP-1 (140 mg/kg) and soil borehole 24SS-1 (210 mg/kg). The relatively low magnitude of the 1995 detections supports the contention that the majority of contaminated soils were removed in late 1991.

4.2.3 Total Organic Carbon

TOC concentrations are a measure of the amount of organic matter sorbed on soil particles or trapped in the interstitial passages of a soil matrix. The TOC concentration in the saturated zone is an important parameter used to estimate the amount of contaminant that could potentially be sorbed to the aquifer matrix. Sorption results in retardation of the contaminant plume migration relative to the average advective groundwater velocity.

Samples for TOC analysis were collected in sandy material in the vicinity of the water table at 24MP-3, 24MP-4, 24MP-6, and 24MP-7. To avoid interference from carbon present in fuel hydrocarbons, these locations were selected because historical data and field observations indicated that little or no hydrocarbon contamination was present. The TOC content of the soil at these locations ranged from less than 0.06 percent to 2.68 percent, and averaged 0.54 percent (Table 4.3). The calculated average assumes that the TOC content of the sample from 24MP-7 was zero, and that the TOC content of the sample from 24MP-6 was 1.8 percent, which is the average of the primary and duplicate results for this location.

4.3 GROUNDWATER CHEMISTRY

Biodegradation of fuel hydrocarbons can occur when an indigenous population of hydrocarbon-degrading microorganisms is present in the aquifer and sufficient concentrations of electron acceptors and nutrients, including fuel hydrocarbons, are available to these organisms. Three lines of evidence can be used to document the occurrence of natural attenuation:

- Geochemical evidence;
- Documented loss of contaminant mass at the field scale; and
- Laboratory microcosm studies.

The first line of evidence (geochemical evidence) is used herein to support the occurrence of natural attenuation, as described in the following sections. Because this line of evidence strongly suggests that natural attenuation is occurring at this site, laboratory microcosm studies were not deemed necessary. A review of historical groundwater quality data indicates that dissolved BTEX concentrations have not always

TABLE 4.3
SOIL TOTAL ORGANIC CARBON RESULTS
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Sampling Location	Depth (feet bgs)	Total Organic Carbon ^{a/} (%)
24MP-3	3 - 5	0.25
24MP-4	3 - 5	0.15
24MP-6	4 - 6	2.68
24MP-7	2 - 4	<0.06
24MP-16 ^{b/}	4 - 6	0.87

a/ Moisture adjusted result.

b/ Duplicate of 24MP-6, 4-6 bgs.

NOTE: Analysis method was SW9060, modified.

consistently decreased with time. Therefore, loss of mass at the field scale cannot be documented with certainty using historical concentration data. However, as described in Section 5.3.5, field data do indicate that biodegradation of dissolved BTEX is occurring.

4.3.1 Dissolved Hydrocarbon Contamination

Laboratory analytical results for groundwater samples collected during previous site investigations (CH2M Hill, 1990 and 1991a) revealed the presence of dissolved fuel hydrocarbon contamination in the shallow saturated zone. Historical groundwater quality results are contained in Appendix A. Groundwater samples collected in 1994 by Enserch Environmental (1994a and 1994b) and in March 1995 by Parsons ES personnel confirmed the presence of dissolved BTEX contamination. Table 4.4 summarizes 1995 groundwater contaminant data for these samples.

4.3.1.1 Dissolved BTEX Contamination

Figure 4.4 is an isopleth map showing the distribution of total BTEX dissolved in groundwater in March 1995. Where nested monitoring points or wells are present, isopleths are drawn using the maximum concentration detected at that location. As shown in Table 4.4 and Figure 4.4, the maximum dissolved BTEX concentrations were always detected in the shallow monitoring well or point. The maximum observed total BTEX concentration was 2,840 $\mu\text{g/L}$ at monitoring point 24MP-1S, which is located adjacent to the former eastern drain field. Elsewhere, the detected total BTEX concentrations ranged from 0.4 $\mu\text{g/L}$ at monitoring point 24MP-2D to 514 $\mu\text{g/L}$ at monitoring well MD24-6. On the basis of the work of Smith *et al.* (1981), the maximum dissolved BTEX concentration that could result from the equilibrium partitioning of BTEX compounds from fresh JP-4 into groundwater is approximately 22,600 $\mu\text{g/L}$. Using the mass fraction of BTEX compounds in the mobile LNAPL sample collected at the site, the maximum expected equilibrium partitioning of BTEX compounds into the groundwater is approximately 18 $\mu\text{g/L}$. Equilibrium partitioning calculations are contained in Appendix D. The substantially higher maximum concentration detected in site groundwater (2,840 $\mu\text{g/L}$) suggests that LNAPL containing higher BTEX concentrations than were measured in the LNAPL sample is present.

The plume appears to be elongated toward the south, as indicated by the detection of 180 $\mu\text{g/L}$ benzene in monitoring point 24PZ-1S (Figure 4.4). The detection of benzene at this location was confirmed when this monitoring point was resampled in October 1995. Benzene was detected in the October sample at a concentration of 210 $\mu\text{g/L}$, and, as with the March 1995 sample, the remaining BTEX compounds were not detected. The lack of toluene, ethylbenzene, and xylene detections at this location may be reflective of the fact that these compounds tend to sorb more readily to aquifer materials, resulting in a slower migration rate. The probable abundance of plant root (i.e., organic) material near the water table beneath the forested area south of the EMTL would tend to enhance retardation of the BTEX compounds. The southern extent of the plume is not known. Available chemical and hydrogeologic data suggest that the plume migration direction beyond monitoring point 24PZ-1 is southerly to southeasterly; however, a monitoring point was not installed in the forested area south of 24PZ-1 due to the density of the vegetation and resulting access difficulty.

1995 GROUNDWATER QUALITY DATA FOR FUEL-RELATED COMPOUNDS AND TOC

SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Sample Location	Sample Date	Benzene ($\mu\text{g/L}$) ^g	Toluene ($\mu\text{g/L}$)	Ethylbenzene ($\mu\text{g/L}$)	Total Xylenes ($\mu\text{g/L}$)	Total BTX ($\mu\text{g/L}$)	TVH ^u (mg/L) ^h	TOC ^h (mgC/L) ⁱ	Chloro- Benzene ($\mu\text{g/L}$)	1,3,5- TMB ^u ($\mu\text{g/L}$)	1,2,4- TMB ^u ($\mu\text{g/L}$)	1,2,3- TMB ^u ($\mu\text{g/L}$)	1,2,3,4- TMB ^u ($\mu\text{g/L}$)
24MP-1S	3/23/95	220	1800	130	690	2840	13	NA ^j	62	65	ND ^v	ND	73
24MP-1D	3/22/95	15	ND	ND	0.5	15.5	ND	NA	1	ND	ND	ND	ND
24MP-2S	3/22/95	3.9	14	14	2.5	34.4	1	NA	1.8	10	29	7.8	ND
24MP-2D	3/22/95	0.4	ND	ND	ND	0.4	ND	NA	0.9	ND	ND	ND	ND
24MP-3S	3/20/95	ND	3.6 ^u	ND	ND	3.6 ^j	ND	NA	ND	ND	ND	ND	0.7J
24MP-3D	3/20/95	ND	ND	ND	ND	ND	ND	NA	ND	ND	ND	ND	0.8J
24MP-4S	3/23/95	ND	9.3	ND	ND	9.3	ND	NA	ND	ND	ND	ND	ND
24MP-5S	3/20/95	ND	9.3	ND	ND	9.3	ND	NA	ND	ND	ND	ND	ND
24MP-5S dup	3/20/95	ND	9	ND	ND	9	NA	NA	ND	ND	ND	ND	ND
24MP-5D	3/23/95	ND	ND	ND	ND	ND	ND	NA	0.8	ND	ND	ND	0.8
24MP-6S	3/24/95	ND	ND	ND	ND	ND	ND	30.1	4.1	ND	ND	ND	ND
24MP-7S	3/16/95	ND	3.1J	ND	ND	3.1J	ND	NA	ND	ND	ND	ND	ND
24MP-7D	3/16/95	ND	ND	ND	ND	ND	ND	NA	ND	ND	ND	ND	ND
24MP-8S	3/20/95	ND	5.4	ND	ND	5.4	ND	NA	ND	ND	ND	ND	ND
24MP-8S dup	3/20/95	ND	5.6	ND	ND	5.6	NA	NA	ND	ND	ND	ND	ND
24MP-8D	3/20/95	ND	ND	ND	ND	ND	ND	NA	ND	ND	ND	ND	ND
24MP-9S	3/15/95	3.0J	4.5	ND	ND	7.5J	0.6	NA	ND	ND	0.4J	ND	16
24MP-9D	3/15/95	ND	ND	ND	ND	ND	0.3	NA	ND	ND	ND	ND	ND
24MP-9D dup	3/15/95	ND	ND	ND	ND	ND	NA	NA	ND	ND	ND	ND	ND
24MP-10S	3/15/95	ND	22	ND	ND	22	ND	NA	ND	ND	ND	ND	ND
24MP-10D	3/15/95	ND	ND	ND	ND	ND	ND	NA	ND	ND	ND	ND	ND
24MP-10D dup	3/15/95	ND	ND	ND	ND	ND	NA	NA	ND	ND	ND	ND	ND
MD24-1	3/23/95	1.8	ND	ND	ND	1.8	ND	NA	1	ND	ND	ND	ND
MD24-2	3/23/95	20	0.9	0.6	0.6	22.1	ND	NA	0.8B ^u	ND	ND	ND	1.7
MD24-3	3/23/95	ND	ND	ND	ND	ND	ND	34.6	0.8	ND	ND	ND	ND
MD24-4	3/23/95	ND	ND	ND	ND	ND	ND	NA	0.7B	ND	ND	ND	0.8
MD24-4 dup	3/23/95	ND	ND	ND	ND	ND	ND	NA	0.6	ND	ND	ND	ND
MD24-5	3/23/95	ND	0.5	ND	ND	0.5	ND	5.52	ND	ND	ND	ND	ND
MD24-6A	3/31/95	3.2	ND	ND	ND	3.2	NA	NA	1.2	0.5	ND	ND	1.2
MD24-6	3/31/95	480	2.2	25	6.7	513.9	NA	NA	1.3	0.5	1	2.3	8.5
MD24-7	3/21/95	3.1J	ND	ND	ND	3.1J	ND	NA	ND	ND	ND	ND	0.7J
MD24-7 dup	3/21/95	3.2J	ND	ND	ND	3.2J	NA	NA	ND	ND	ND	ND	ND

TABLE (Continued)
1995 GROUNDWATER QUALITY DATA FOR FUEL-RELATED COMPOUNDS AND TOC
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Sample Location	Sample Date	Benzene (µg/L) ^{g/}	Toluene (µg/L)	Ethylbenzene (µg/L)	Total Xylenes (µg/L)	Total BTX (µg/L)	TVH ^{a/} (mg/L) ^{j/}	TOC ^{b/} (mgC/L) ^{i/}	Chloro- Benzene (µg/L)	1,3,5- TMB ^{d/} (µg/L)	1,2,4- TMB ^{d/} (µg/L)	1,2,3- TMB ^{d/} (µg/L)	1,2,3,4 TEMB ^{f/} (µg/L)
MD24-8	3/22/95	ND	ND	ND	ND	ND	ND	NA	ND	ND	ND	ND	ND
MD24-9	3/20/95	ND	ND	ND	0.5JB	0.5JB	ND	NA	ND	ND	ND	ND	ND
MD24-10A	3/31/95	ND	ND	ND	ND	ND	NA	NA	ND	0.8	ND	ND	ND
MD24-10	3/31/95	ND	ND	ND	ND	ND	NA	NA	ND	ND	ND	ND	ND
24PZ-1S	3/24/95	180	ND	ND	ND	180	0.5	NA	ND	ND	ND	ND	ND
24PZ-1S	7/21/95	210	ND	ND	ND	210	ND	NA	0.6	ND	0.6	ND	ND
24PZ-1D	3/24/95	2.3	ND	ND	ND	2.3	ND	NA	0.6	ND	ND	ND	ND
24PZ-2S	7/21/95	ND	ND	ND	ND	ND	NA	NA	ND	ND	ND	ND	ND
24PZ-2S dup	7/21/95	ND	ND	ND	ND	ND	NA	NA	ND	ND	ND	ND	ND
24PZ-3S	7/21/95	ND	ND	ND	ND	ND	NA	NA	ND	ND	ND	ND	ND
24PZ-3D	7/21/95	ND	ND	ND	ND	ND	NA	NA	ND	ND	ND	ND	ND
24PZ-4S	7/21/95	ND	ND	ND	ND	ND	NA	NA	ND	ND	ND	ND	ND
24PZ-5S	7/21/95	ND	ND	ND	ND	ND	NA	NA	ND	ND	ND	ND	ND
RINSEATE BLANK	3/31/95	ND	ND	ND	ND	ND	NA	NA	ND	ND	ND	ND	ND
RINSEATE BLANK	7/21/95	ND	ND	ND	ND	ND	NA	NA	ND	ND	ND	ND	ND
FIELD BLANK	3/15/95	ND	ND	ND	ND	ND	ND	NA	ND	ND	ND	ND	ND
FIELD BLANK	3/31/95	ND	ND	ND	ND	ND	NA	NA	ND	ND	ND	ND	ND

a/ TVH = total volatile hydrocarbons.

b/ TOC = total organic carbon.

c/ 1,3,5 TMB = 1,3,5 trimethylbenzene.

d/ 1,2,4 TMB = 1,2,4 trimethylbenzene.

e/ 1,2,3 TMB = 1,2,3 trimethylbenzene.

f/ 1,2,3,4 TEMB = 1,2,3,4 tetramethylbenzene.

g/ µg/L = micrograms per liter.

h/ mg/L = milligrams per liter.

i/ mgC/L = milligrams carbon per liter.

j/ NA = compound not analyzed for.

k/ ND = compound not detected.

l/ J = laboratory estimate.

m/ B = compound detected in associated laboratory blank sample.

NOTE: Analysis methods included SW8015M for TEH and TVH, E415.1 for TOC, and SW8020 for aromatic volatile

organic compounds, including TMB and TEMB compounds.

Therefore, the southerly plume extent depicted on Figure 4.4 is estimated. The maximum dissolved BTEX detection deeper in the surficial aquifer was 15.5 µg/L at 24MP-1D (Table 4.4), indicating that the BTEX contamination is primarily present in the upper portion of the surficial aquifer.

The dissolved BTEX data suggest that an additional, relatively minor contamination source may be present in the vicinity of monitoring point 24MP-5, and that contamination from this area has migrated to the southwest to 24MP-7 and 24MP-8 (Figure 4.4). A second, minor contamination source may be present east to northeast of the EMTL, near or upgradient from monitoring point 24MP-4S.

The maximum dissolved BTEX concentration detected during previous investigations was 225 µg/L, measured in December 1988 at monitoring well MD24-01 (Appendix A). This is substantially lower than the maximum value detected in March 1995 of 2,840 µg/L. There are a number of possible reasons for this discrepancy. The wells sampled prior to March 1995 were adjacent to the probable primary source area rather than within it. In addition, monitoring wells MD24-1 through MD24-4 are screened from 10 to 20 feet bgs, which is most likely below the zone containing the highest dissolved BTEX concentrations. Monitoring wells MD24-5 through MD25-10 are screened between 2 and 12 feet bgs. Differences in sampling methods may also have contributed to the observed discrepancy. During the aquifer pumping test performed in well P-1 in August 1989 however, total BTEX concentrations detected in the pumped water ranged from 1,210 µg/L to 1,710 µg/L (CH2M Hill, 1990). The pumping well was located immediately adjacent to a probable major source area (the former eastern drain field), and was probably drawing water from that area (as well as other surrounding areas) during the test.

Multiple groundwater sampling events have occurred at Site OT 24, beginning in December 1988. BTEX concentrations in wells MD24-1 and MD24-6A have generally decreased over time. BTEX concentrations in well MD24-2 fluctuated up and down between December 1988 and May 1994, and have steadily decreased since May 1994. BTEX concentrations in well MD24-6 also have fluctuated erratically, with the highest concentration occurring in the most recent (March 1995) sampling event. These data suggest that some reductions in contaminant mass are occurring with time, but the trends are not consistent. The continued presence of LNAPL in the immediate vicinity of the former eastern drain field represents a continuing source of dissolved BTEX that can effectively negate contaminant mass reductions in the source area that may result from biodegradation. Furthermore, it is likely that BTEX dissolution varies seasonally. During relatively wet periods when precipitation percolates through the soil column to the groundwater and the water table is high, increased partitioning of BTEX from both mobile and residual LNAPL into the groundwater may occur. Conversely, BTEX partitioning may be reduced during relatively dry, low water periods.

Florida groundwater quality standards for benzene and total volatile organic aromatics (BTEX) in class G-II groundwater are 1 µg/L and 50 µg/L, respectively [Florida Department of Environmental Protection (DEP), 1994]. March 1995 concentrations of benzene and total volatile organic aromatics exceeded these standards at eight and four locations, respectively (a shallow and deep monitoring well/point pair is considered to represent one location). However, the benzene action level can potentially be raised to 50 µg/L if groundwater is not extracted for potable use within

0.25 mile of the site. [Florida Department of Environmental Regulation (FDER), 1990].

4.3.1.2 Dissolved TPH Contamination

Groundwater samples collected by Parsons ES were analyzed for TVH using USEPA Method SW8015, modified. The TVH results correlate well with the BTEX results, with the maximum TVH concentration of 13 mg/L detected at monitoring point 24MP-1S (Table 4.4). The remaining TVH detections did not exceed 1 mg/L.

4.3.1.3 Chlorinated Volatile Organic Compounds

Table 4.5 contains analytical data for chlorinated VOCs and ethylene (which is a byproduct of chlorinated solvent degradation). The groundwater samples collected in March 1995 were analyzed for tetrachloroethene (PCE), trichloroethene (TCE), cis-1,2-dichloroethene (cis-1,2-DCE), trans-1,2-DCE, 1,1-DCE, and vinyl chloride using USEPA Method RSKSOP-148. The analyses were performed at the USEPA NRMRL. The VOCs, PCE and TCE were each detected in one well at concentrations of 1.1 and 2.6 µg/L, respectively. These concentrations are below the USEPA (1994) MCL for these compounds of 5 µg/L and the Florida drinking water standards of 3 µg/L (FDER, 1989). The VOCs cis-1,2-DCE and vinyl chloride were detected in five wells and six wells, respectively. Detected concentrations of cis-1,2-DCE ranged from 1.0 µg/L to 6.8 µg/L, and vinyl chloride concentrations ranged from 1.0 to 20.8 µg/L. The USEPA (1994) MCLs for cis-1,2-DCE and vinyl chloride are 70 µg/L and 2 µg/L, respectively. The Florida drinking water standard for vinyl chloride is 1 µg/L, and the Florida guideline (not promulgated) for cis-1,2-DCE is 4.2 µg/L (FDER, 1989). The highest DCE and vinyl chloride concentrations occurred in the sample from monitoring point 24MP-1S, which also had the highest dissolved BTEX concentration. The second highest vinyl chloride concentration (16.4 µg/L) was detected in well 24MW-6A, which is screened deeper in the surficial aquifer downgradient from the source area. Vinyl chloride and cis-1,2-DCE were also detected at monitoring points 24PZ-1S/1D, indicating that these compounds have migrated at least 200 feet in a southerly direction from the source area. Ethylene, which is a byproduct of the degradation of chlorinated VOCs, was detected only in the sample from MD24-6A at a concentration of 1J µg/L. The "J" qualifier indicates that the detected concentration is an estimated value.

Chlorinated VOCs detected by CH2M Hill (1990 and 1991a) and Enserch Environmental (1994a and 1994b) during previous Hydrocone® sampling, monitoring well sampling, and sampling of the pumping test discharge water (and the maximum detected concentration) have included TCE (2.3 µg/L), 1,1-DCE (2.5 µg/L), cis/trans-1,2-DCE (1.9 µg/L), 1,1-DCA (178 µg/L), vinyl chloride (59.4 µg/L), methylene chloride (29 µg/L), acetone (19 µg/L), carbon disulfide (2 µg/L), and 2-butanone (methyl ethyl ketone) (25 µg/L). CH2M Hill and Enserch Environmental groundwater quality data are included in Appendix A. According to CH2M Hill (1990), the widespread detection of low levels of methylene chloride is indicative of laboratory-introduced contamination. Acetone was reportedly used at the EMTL, but detections of this compound may also be at least partly representative of laboratory-introduced contamination.

TABLE 4.5
1995 GROUNDWATER QUALITY DATA FOR CHLORINATED VOLATILE
ORGANIC COMPOUNDS AND ETHYLENE
SITE 0T 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Sample Identification	PCE ^{a/} (ppb) ^{f/}	TCE ^{b/} (ppb)	1,1-DCE ^{c/} (ppb)	Trans-1,2-DCE ^{d/} (ppb)	Cis-1,2-DCE ^{e/} (ppb)	Vinyl Chloride (ppb)	Ethylene (ppm) ^{g/}
24MP-1S	1.1	<1.0 ^{b/}	ND ^{i/}	ND	6.8	20.7	<0.003 ^{k/}
24MP-1S dup	1.0	ND	ND	ND	6.2	20.8	NA ^{j/}
24MP-1D	ND	ND	ND	ND	1.1	ND	ND
24MP-2S	ND	ND	ND	ND	ND	ND	ND
24MP-2D	ND	ND	ND	ND	<1.0 ^{b/}	ND	ND
24MP-3S	ND	ND	ND	ND	ND	ND	ND
24MP-3D	ND	ND	ND	ND	<1.0 ^{b/}	ND	ND
24MP-4S	ND	ND	ND	ND	ND	ND	NA
24MP-5S	ND	ND	ND	ND	ND	ND	ND
24MP-5D	ND	ND	ND	ND	ND	ND	ND
24MP-6S	ND	ND	ND	ND	ND	ND	ND
24MP-7S	ND	ND	ND	ND	ND	ND	ND
24MP-7D	ND	ND	ND	ND	ND	ND	ND
24MP-7D dup	ND	ND	ND	ND	ND	ND	ND
24MP-8S	ND	ND	ND	ND	ND	ND	ND
24MP-8D	ND	ND	ND	ND	ND	ND	ND
24MP-9S	ND	ND	ND	ND	ND	ND	ND
24MP-9D	ND	ND	ND	ND	1.8	ND	ND
24MP-10S	ND	ND	ND	ND	ND	ND	ND
24MP-10D	ND	ND	ND	ND	ND	ND	ND
24PZ-1S	ND	ND	ND	ND	1.0	2.8	ND
24PZ-1S dup	ND	ND	ND	ND	<1.0 ^{b/}	2.6	NA
24PZ-1D	ND	ND	ND	ND	<1.0 ^{b/}	1.0	ND
MD24-1	ND	ND	ND	ND	<1.0 ^{b/}	1.0 ^{b/}	ND
MD24-2	ND	2.6	ND	ND	1.4	3.4	ND
MD24-3	ND	ND	ND	ND	ND	ND	ND
MD24-4	ND	ND	ND	ND	ND	ND	ND
MD24-4 dup	ND	ND	ND	ND	<1.0 ^{b/}	ND	ND
MD24-5	ND	ND	ND	ND	ND	ND	ND
MD24-6	ND	ND	ND	ND	<1.0 ^{b/}	<1.0 ^{b/}	ND
MD24-6A	ND	ND	ND	ND	ND	16.4	0.001J ^{k/}
MD24-7	ND	ND	ND	ND	ND	1.2	ND
MD24-8	ND	ND	ND	ND	ND	ND	ND
MD24-9	ND	ND	ND	ND	ND	ND	ND
MD24-10	ND	ND	ND	ND	<1.0 ^{b/}	ND	ND
MD24-10A	ND	ND	ND	ND	ND	ND	ND

a/ PCE = Tetrachloroethene.

b/ TCE = Trichloroethene.

c/ 1,1-DCE = 1,1 Dichloroethene.

d/ Trans-1,2-DCE = Trans-1,2-Dichloroethene.

e/ Cis-1,2-DCE = Cis-1,2-Dichloroethene.

f/ ppb = parts per billion.

g/ ppm = parts per million.

h/ Compound detected below lower limit of quantitation.

i/ ND = compound not detected.

j/ NA = compound not analyzed for.

k/ J = laboratory estimated value.

NOTE: Analysis methods included Robert S. Kerr Standard Operating Procedure (RSKSOP)-148 for volatile organic compounds and RSKSOP-175 for ethylene.

4.3.2 Inorganic Chemistry and Geochemical Indicators of BTEX Biodegradation

Microorganisms obtain energy for cell production and maintenance by catalyzing the transfer of electrons from electron donors to electron acceptors. This results in the oxidation of the electron donor and the reduction of the electron acceptor. Electron donors at the site are natural organic carbon and fuel hydrocarbon compounds. Fuel hydrocarbons are completely degraded or detoxified if they are utilized as the primary electron donor for microbial metabolism (Bouwer, 1992). Electron acceptors are elements or compounds that occur in relatively oxidized states, and typically can include oxygen, nitrate, ferric iron, sulfate, and carbon dioxide. Microorganisms preferentially utilize electron acceptors while metabolizing fuel hydrocarbons (Bouwer, 1992). DO is utilized first as the prime electron acceptor. After the DO is consumed, anaerobic microorganisms typically use electron acceptors (as available) in the following order of preference: nitrate, ferric iron hydroxide, sulfate, and finally carbon dioxide. Because the biodegradation of fuel hydrocarbons should deplete the concentrations of these electron acceptors, construction of isopleth maps depicting their concentrations can provide evidence of whether biodegradation is occurring, and the degree to which it is occurring.

During anaerobic biodegradation, there is an increase in the concentrations of metabolic byproducts derived from the microbial degradation of fuel hydrocarbons. Metabolic byproducts include ferrous iron produced during iron reduction, and methane produced during methanogenesis, which uses carbon dioxide as the electron acceptor. Therefore, isopleth maps depicting the concentrations of these byproducts can provide additional evidence of biodegradation.

The driving force of BTEX degradation is electron transfer and is quantified by the Gibbs free energy of the reaction (ΔG_r) (Stumm and Morgan, 1981; Bouwer, 1994; Godsey, 1994). The value of ΔG_r represents the quantity of free energy consumed or yielded to the system during the reaction. Table 4.6 lists stoichiometry of the redox equations involving BTEX and the resulting ΔG_r . Although thermodynamically favorable, most of the reactions involved in BTEX oxidation cannot proceed abiotically because of the lack of activation energy. Microorganisms are capable of providing the necessary activation energy; however, they will facilitate only those redox reactions that have a net yield of energy (i.e., $\Delta G_r < 0$).

Depending on the types and concentrations of electron acceptors present (e.g., nitrate, ferric iron, sulfate, carbon dioxide), pH conditions, and redox potential, anaerobic biodegradation can occur by denitrification, ferric iron reduction, sulfate reduction, or methanogenesis. Other, less common anaerobic degradation mechanisms such as manganese reduction may dominate if the physical and chemical conditions in the subsurface favor use of these electron acceptors. Anaerobic destruction of BTEX compounds is associated with the accumulation of fatty acids, production of methane, solubilization of iron, and reduction of nitrate and sulfate (Cozzarelli *et al.*, 1990; Wilson *et al.*, 1990). In addition, an increase in alkalinity is often observed when BTEX compounds are being biodegraded. Environmental conditions and microbial competition will ultimately determine which processes will dominate. Vroblesky and Chapelle (1994) show that the dominant terminal electron accepting process can vary both temporally and spatially in an aquifer with fuel hydrocarbon contamination.

TABLE 4.6
COUPLED OXIDATION REACTIONS FOR BTEX COMPOUNDS
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Coupled Benzene Oxidation Reactions	ΔG°_r (kcal/mole Benzene)	ΔG°_r (kJ/mole Benzene)	Stoichiometric Mass Ratio of Electron Acceptor to Compound
$7.5O_2 + C_6H_6 \Rightarrow 6CO_{2,g} + 3H_2O$ <i>Benzene oxidation / aerobic respiration</i>	-765.34	-3202	3.07:1
$6NO_3^- + 6H^+ + C_6H_6 \Rightarrow 6CO_{2,g} + 6H_2O + 3N_{2,g}$ <i>Benzene oxidation / denitrification</i>	-775.75	-3245	4.77:1
$3.75NO_3^- + C_6H_6 + 7.5H^+ + 0.75H_2O \Rightarrow 6CO_2 + 3.75NH_4^+$ <i>Benzene oxidation / nitrate reduction</i>	-524.1	-2193	2.98:1
$60H^+ + 30Fe(OH)_3 \cdot n + C_6H_6 \Rightarrow 6CO_2 + 30Fe^{2+} + 78H_2O$ <i>Benzene oxidation / iron reduction</i>	-560.10	-2343	21.5:1 ^{a/}
$75H^+ + 3.75SO_4^{2-} + C_6H_6 \Rightarrow 6CO_{2,g} + 3.75H_2S^o + 3H_2O$ <i>Benzene oxidation / sulfate reduction</i>	-122.93	-514.3	4.61:1
$4.5H_2O + C_6H_6 \Rightarrow 2.25CO_{2,g} + 3.75CH_4$ <i>Benzene oxidation / methanogenesis</i>	-32.40	-135.6	0.77:1 ^{b/}

Coupled Toluene Oxidation Reactions	ΔG°_r (kcal/mole Toluene)	ΔG°_r (kJ/mole Toluene)	Stoichiometric Mass Ratio of Electron Acceptor to Compound
$9O_2 + C_6H_5CH_3 \Rightarrow 7CO_{2,g} + 4H_2O$ <i>Toluene oxidation / aerobic respiration</i>	-913.76	-3823	3.13:1
$7.2NO_3^- + 7.2H^+ + C_6H_5CH_3 \Rightarrow 7CO_{2,g} + 7.6H_2O + 3.6N_{2,g}$ <i>Toluene oxidation / denitrification</i>	-926.31	-3875	4.85:1
$72H^+ + 36Fe(OH)_3 \cdot n + C_6H_5CH_3 \Rightarrow 7CO_2 + 36Fe^{2+} + 94H_2O$ <i>Toluene oxidation / iron reduction</i>	-667.21	-2792	21.86:1 ^{a/}
$9H^+ + 4.5SO_4^{2-} + C_6H_5CH_3 \Rightarrow 7CO_{2,g} + 4.5H_2S^o + 4H_2O$ <i>Toluene oxidation / sulfate reduction</i>	-142.86	-597.7	4.7:1
$5H_2O + C_6H_5CH_3 \Rightarrow 2.5CO_{2,g} + 4.5CH_4$ <i>Toluene oxidation / methanogenesis</i>	-34.08	-142.6	0.78:1 ^{b/}

TABLE 4.6 (Continued)
COUPLED OXIDATION REACTIONS FOR BTEX COMPOUNDS
SITE OT 24

INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Coupled Ethylbenzene Oxidation Reactions	ΔG°_r (kcal/mole Ethyl- benzene)	ΔG°_r (kJ/mole Ethyl- benzene)	Stoichiometric Mass Ratio of Electron Acceptor to Compound
$10.5 O_2 + C_6H_5C_2H_5 \Rightarrow 8 CO_{2,s} + 5 H_2O$ <i>Ethylbenzene oxidation / aerobic respiration</i>	-1066.13	-4461	3.17:1
$8.4 NO_3 + 8.4 H^+ + C_6H_5C_2H_5 \Rightarrow 8 CO_{2,s} + 9.2 H_2O + 4.2 N_{2,s}$ <i>Ethylbenzene oxidation / denitrification</i>	-1080.76	-4522	4.92:1
$84 H^+ + 42 Fe(OH)_3, a + C_6H_5C_2H_5 \Rightarrow 8 CO_2 + 42 Fe^{2+} + 110 H_2O$ <i>Ethylbenzene oxidation / iron reduction</i>	-778.48	-3257	22:1 ^{a/}
$10.5 H^+ + 5.25 SO_4^{2-} + C_6H_5C_2H_5 \Rightarrow 8 CO_{2,s} + 5.25 H_2S^o + 5 H_2O$ Ethylb <i>enzene oxidation / sulfate reduction</i>	-166.75	-697.7	4.75:1
$5.5 H_2O + C_6H_5C_2H_5 \Rightarrow 2.75 CO_{2,s} + 5.25 CH_4$ <i>Ethylbenzene oxidation / methanogenesis</i>	-39.83	-166.7	0.79:1 ^{b/}

Coupled m-Xylene Oxidation Reactions	ΔG°_r (kcal/mole m-xylene)	ΔG°_r (kJ/mole m-xylene)	Stoichiometric Mass Ratio of Electron Acceptor to Compound
$10.5 O_2 + C_6H_4(CH_3)_2 \Rightarrow 8 CO_{2,s} + 5 H_2O$ <i>m-Xylene oxidation / aerobic respiration</i>	-1063.25	-4448	3.17:1
$8.4 NO_3 + 8.4 H^+ + C_6H_4(CH_3)_2 \Rightarrow 8 CO_{2,s} + 9.2 H_2O + 4.2 N_{2,s}$ <i>m-Xylene oxidation / denitrification</i>	-1077.81	-4509	4.92:1
$84 H^+ + 42 Fe(OH)_3, a + C_6H_4(CH_3)_2 \Rightarrow 8 CO_2 + 42 Fe^{2+} + 110 H_2O$ <i>m-Xylene oxidation / iron reduction</i>	-775.61	-3245	22:1 ^{a/}
$10.5 H^+ + 5.25 SO_4^{2-} + C_6H_4(CH_3)_2 \Rightarrow 8 CO_{2,s} + 5.25 H_2S^o + 5 H_2O$ <i>m-Xylene oxidation / sulfate reduction</i>	-163.87	-685.6	4.75:1
$5.5 H_2O + C_6H_4(CH_3)_2 \Rightarrow 2.75 CO_{2,s} + 5.25 CH_4$ <i>m-Xylene oxidation / methanogenesis</i>	-36.95	-154.6	0.79:1 ^{b/}

^{a/} Mass of ferrous iron produced during microbial respiration.

^{b/} Mass of methane produced during microbial respiration.

On the basis of available data, biodegradation of fuel hydrocarbons at Site OT 24 is occurring, and concentrations of methane and sulfate indicate that methanogenesis and sulfate reduction are the primary pathways for biodegradation. Concentrations of DO and ferrous iron, as well as measured redox potentials, also support the occurrence of biodegradation, but the trends are less apparent. Alkalinity data also support the occurrence of biodegradation. Geochemical parameters, and their relation to the distribution of dissolved BTEX in groundwater, are discussed in the following sections.

4.3.2.1 Dissolved Oxygen

DO concentrations were measured at monitoring wells and monitoring points in March 1995 (Table 4.7). Figure 4.5 is an isopleth map showing the distribution of DO concentrations in groundwater. The generally low DO concentrations both inside and outside of the contaminant plume indicate that the groundwater system is naturally low in DO, that DO is not an important electron acceptor at this site, and that the degradation mechanisms operating at the site are primarily anaerobic. Natural DO concentrations in water typically decrease as the water temperature increases. In the immediate vicinity of the EMTL and extending to the southwest, DO concentrations are mostly less than 0.1 mg/L. Within the area characterized by elevated BTEX concentrations (greater than 10 µg/L), shallow DO concentrations ranged from 0.06 mg/L at monitoring point 24MP-2S and monitoring well MD24-2 to 0.79 mg/L at 24PZ-1S, and increased with distance downgradient from the EMTL. The average (mean) DO concentration within the 10-µg/L BTEX isopleth was 0.24 mg/L. DO concentrations in areas that are outside or on the margin of the BTEX plume (24MP-6S, MD24-3, MD24-4, MD24-5, MD24-8, MD24-10, 24PZ-2S, 24PZ-3S, 24PZ-4S, and 24PZ-5S) ranged from 0.02 mg/L to 1.54 mg/L, and averaged 0.56 mg/L. DO concentrations measured in monitoring wells or points screened in deeper portions of the surficial aquifer ranged from 0.09 mg/L at 24MP-10D to 2.63 mg/L at 24PZ-3D and averaged 0.59 mg/L.

The stoichiometry of BTEX mineralization to carbon dioxide and water caused by aerobic microbial biodegradation is presented in Table 4.6. The average mass ratio of oxygen to total BTEX is approximately 3.14 to 1. This translates to the mineralization of approximately 0.32 mg of BTEX for every 1.0 mg of DO consumed. With an average shallow groundwater DO concentration outside or on the margins of the BTEX plume of 0.56 mg/L, and an average DO concentration within the plume of 0.24 mg/L, the shallow groundwater at this site may have the capacity to assimilate a maximum of 0.10 mg/L (100 µg/L) of total BTEX through aerobic biodegradation. This may be a conservative estimate of the assimilative capacity of DO because microbial cell mass production was not taken into account by the stoichiometry presented in Table 4.6.

When cell mass production is accounted for, the mineralization of benzene to carbon dioxide and water is given by:

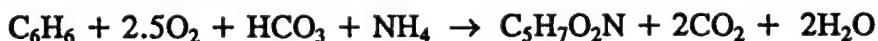


TABLE 4.7
1995 GROUNDWATER GEOCHEMICAL DATA
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Sample Location	Water Temp (°C) ^d	pH	Conductivity (µs/cm) ^d	Dissolved Oxygen (mg/L) ^d	Redox Potential (mV) ^d	Total Alkalinity (mg/L)	Chloride (mg/L)	Ferrous Iron (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)	Total Iron (mg/L)	Sulfate (mg/L)	Manganese (mg/L)	Sulfide (mg/L)	Ammonia (mg/L)	Carbon Dioxide (mg/L)	Methane (mg/L)
24MP-1S	24.6	6.10	580	0.14	-95.1	240	16.2	3.48	ND ^d	ND	3.63	77	ND	0.175I	NA ^u	160	2.501
24MP-1D	25.6	6.49	1960	0.39	-91.4	340	454	13.05	ND ^d	ND	22.15	2	0.9	ND	3	112	1.788
24MP-1D dup	25.6	6.49	1960	0.39	-91.4	340	NA	13.1	NA	NA	25.4	NA	5.4	0.032	6	112	NA
24MP-2S	24.2	5.61	330	0.06	-211.9	200	15.6	1.74	ND	ND	1.63	22.3	ND	0.499I	7I ^u	<100	9.887
24MP-2D	26.0	6.43	1400	0.20	-79.5	340	291	5.2	ND	ND	10.1	10.5	ND	0.016	3	<100	0.145
24MP-3S	23.5	7.02	490	0.08	-238.3	300	6.51	0.09	ND	ND	0.17	7.63	ND	0.036	0.9	<100	0.97
24MP-3D	25.2	6.84	1650	0.25	-149.7	260	384	4.59	ND	ND	5	30.5	ND	0.019	1	<100	0.182
24MP-4S	30.0	6.84	1080	0.30	-97.4	620	30.6	14.7	ND	ND	17.9	23.5	3	0.043	4	145	0.288
24MP-5S	20.6	6.86	780	1.31	-186.5	395	9.06	0.59	ND	ND	0.63	37.4	ND	0.068	0.6	NA	0.065
24MP-5D	24.1	6.65	1590	0.24	-60.4	340	354	3.09	ND	ND	4.45	17.4	ND	0.017	3	<100	0.075
24MP-6S	21.4	6.82	830	0.11	-139.8	400	42.6	1.73	ND	ND	2.2	8.12	ND	0.037	21	<100	1.045
24MP-7S	21.1	6.90	930	0.19	-106.7	320	115	0.44	ND	ND	0.41	76	ND	0.113	1	<100	NA
24MP-7D	21.0	6.73	3630	0.52	-22.9	300	1130	11.7	ND	ND	18	79.2	3.8	0.021	1	<100	0.033
24MP-8S	23.0	7.06	730	0.10	-171.6	300	98.2	0.36	ND	ND	0.41	38.9	ND	0.058	1	<100	0.125
24MP-8D	25.0	6.65	1690	0.18	-130.6	320	347	2.89	ND	ND	4.53	52.7	ND	0.068	1	<100	0.068
24MP-8D dup	25.0	6.65	1690	0.18	-130.6	320	NA	2.95	NA	NA	4.54	NA	ND	0.059	1	<100	NA
24MP-9S	22.8	6.84	570	0.05	-216.8	300	12.1	1.23	ND	ND	1.13	1.91	ND	0.078	2	<100	3.27
24MP-9D	24.7	6.50	1430	0.13	-84.1	300	329	1.75	ND	ND	2.26	12.1	ND	ND	2	<100	0.053
24MP-10S	22.3	6.53	480	0.14	-118.5	320	4.18	1.53	ND	ND	1.73	3.64	ND	0.057	1	<100	0.696
24MP-10S dup	22.3	6.53	480	0.14	-118.5	320	NA	1.19	NA	NA	1.76	NA	ND	0.036	1	<100	NA
24MP-10D	24.1	6.67	980	0.09	-81.6	340	144	4.9	ND	ND	9.35	5.78	ND	0.016	2	<100	0.06
MD24-1	24.9	6.91	910	0.04	-56.8	420	79.8	0.14	ND	ND	0.37	7.16	ND	0.009	2	<100	0.573
MD24-1 dup	24.9	6.91	910	0.04	-56.8	420	NA	0.09	NA	NA	0.35	NA	ND	0.017	2	<100	NA
MD24-2	25.4	6.77	1330	0.06	-82.5	360	262	3.25	ND	ND	4.62	6.78	ND	0.024	3	<100	1.311
MD24-3	25.2	6.70	1130	0.02	-97.5	280	207	0.17	ND	ND	0.11	18.4	ND	0.105	NA	<100	0.242
MD24-4	24.0	6.59	1390	0.05	-18.7	260	320	0.24	ND	ND	0.49	11.7	ND	0.114	NA	<100	0.266
MD24-4 dup	24.0	6.59	1390	0.05	-18.7	260	326	0.22	ND	ND	0.29	11.7	ND	0.107	NA	<100	0.261
MD24-5	23.7	7.06	450	0.13	-211.4	240	2.94	1.1	ND	ND	2.8	12	ND	0.012	0.2	<100	0.271
MD24-6A	24.6	6.53	2350	0.20	-81.5	320	16.8	0.93	ND	ND	1.62	7.34	ND	0.019	2	<100	0.61
MD24-6	22.1	6.48	770	0.28	-95.9	460	637	1.47	ND	ND	1.44	6.38	ND	0.086	2	120	2.335
MD24-6 dup	22.1	6.48	770	0.28	-95.9	460	NA	1.48	NA	NA	1.44	NA	ND	0.073	2	124	NA
MD24-7	23.3	6.90	630	0.23	-34.4	380	8.77	0.07	ND	ND	0.09	14	ND	0.012	0.4	<100	0.429
MD24-7 dup	23.3	6.90	630	0.23	-34.4	380	8.19	0.03	ND	ND	0.06	13.6	ND	0.013	0.4	<100	0.048
MD24-8	27.1	6.61	510	0.14	-117.9	280	6.55	0.23	ND	ND	0.25	1.39	ND	0.079	1	<100	0.578
MD24-9	24.9	7.66	900	0.30	-76.0	480	30.6	3.35	ND	ND	6.2	28	ND	0.019	1	<100	0.146
MD24-10	22.3	6.67	1110	0.07	-123.6	380	140	0.13	ND	ND	0.12	34.6	ND	0.132	2	<100	0.249

TABLE 4.7 (Continued)
1995 GROUNDWATER GEOCHEMICAL DATA
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Sample Location	Water Temp (°C) ^{a/}	pH	Conductivity (µs/cm) ^{b/}	Dissolved Oxygen (mg/L) ^{c/}	Redox Potential (mV) ^{d/}	Total Alkalinity (mg/L)	Chloride (mg/L)	Ferrous Iron (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)	Total Iron (mg/L)	Sulfate (mg/L)	Manganese (mg/L)	Sulfide (mg/L)	Ammonia (mg/L)	Carbon Dioxide (mg/L)	Methane (mg/L)
MD24-10A	22.9	7.05	1410	2.09	6.4	300	370	0.39	1.09	ND	0.89	10.6	ND	ND	0.3	<100	0.749
24PZ-1S	20.7	6.75	700	0.79	-154.3	360	27.4	0.41	ND	ND	0.65	1.04	ND	0.152	3	<100	4.177
24PZ-1D	22.0	6.82	1140	0.13	-169.0	340	177	1.88	ND	ND	2.51	3.56	ND	0.037	2	<100	0.137
24PZ-2S	29.9	7.02	812	1.21	NA	NA	9.5	0.3	8.2	0.084	NA	34.9	NA	NA	NA	NA	0.008
24PZ-2S dup	29.9	7.02	812	1.21	NA	NA	12.1		8.9	0.089	NA	36.8	NA	NA	NA	NA	0.009
24PZ-3S	28.0	7.26	1380	1.54	NA	6.5	6.5	0.2	ND	ND	NA	5.2	NA	NA	NA	NA	0.21
24PZ-3D							1490	ND	ND	ND	164	164	NA	NA	NA	NA	0.020
24PZ-4S	29.3	7.23	846	1.3	NA	NA	6.9	0.2	13	ND	18.4	18.4	NA	NA	NA	NA	0.033
24PZ-5S	30.2	7.03	1180	4.5	NA	NA	8.1	0.4	ND	ND	NA	5.0	NA	NA	NA	NA	0.34

a/ °C = degrees Centigrade.

b/ µs/cm = microseimens per centimeter.

c/ mg/L = milligrams per liter.

d/ mV = millivolts.

e/ ND = compound not detected.

f/ NA = not analyzed for this parameter.

g/ I = potential turbidity interference.

NOTE: See Table 2.2 for analysis methods.

This equation indicates that 5.0 fewer moles of DO are required to mineralize 1 mole of benzene when cell mass production is taken into account. On a mass basis, the ratio of DO to benzene is given by:

$$\text{Benzene} \quad 6(12) + 1(6) = 78 \text{ gm}$$

$$\text{Oxygen} \quad 2.5(32) = 80 \text{ gm}$$

$$\text{Mass Ratio of Oxygen to Benzene} = 80/78 = 1.03:1$$

On the basis of these stoichiometric relationships, 1.03 mg of oxygen is required to mineralize 1 mg of benzene. Similar calculations can be made for toluene, ethylbenzene, and the xylenes. Based on these calculations, approximately 0.97 mg of BTEX is mineralized to carbon dioxide and water for every 1.0 mg of DO consumed. With an average background DO concentration of 0.56 mg/L and an average DO concentration within the plume of 0.24 mg/L, the shallow groundwater at this site may have the capacity to assimilate 0.31 mg/L (310 µg/L) of total BTEX if microbial cell mass production is taken into account.

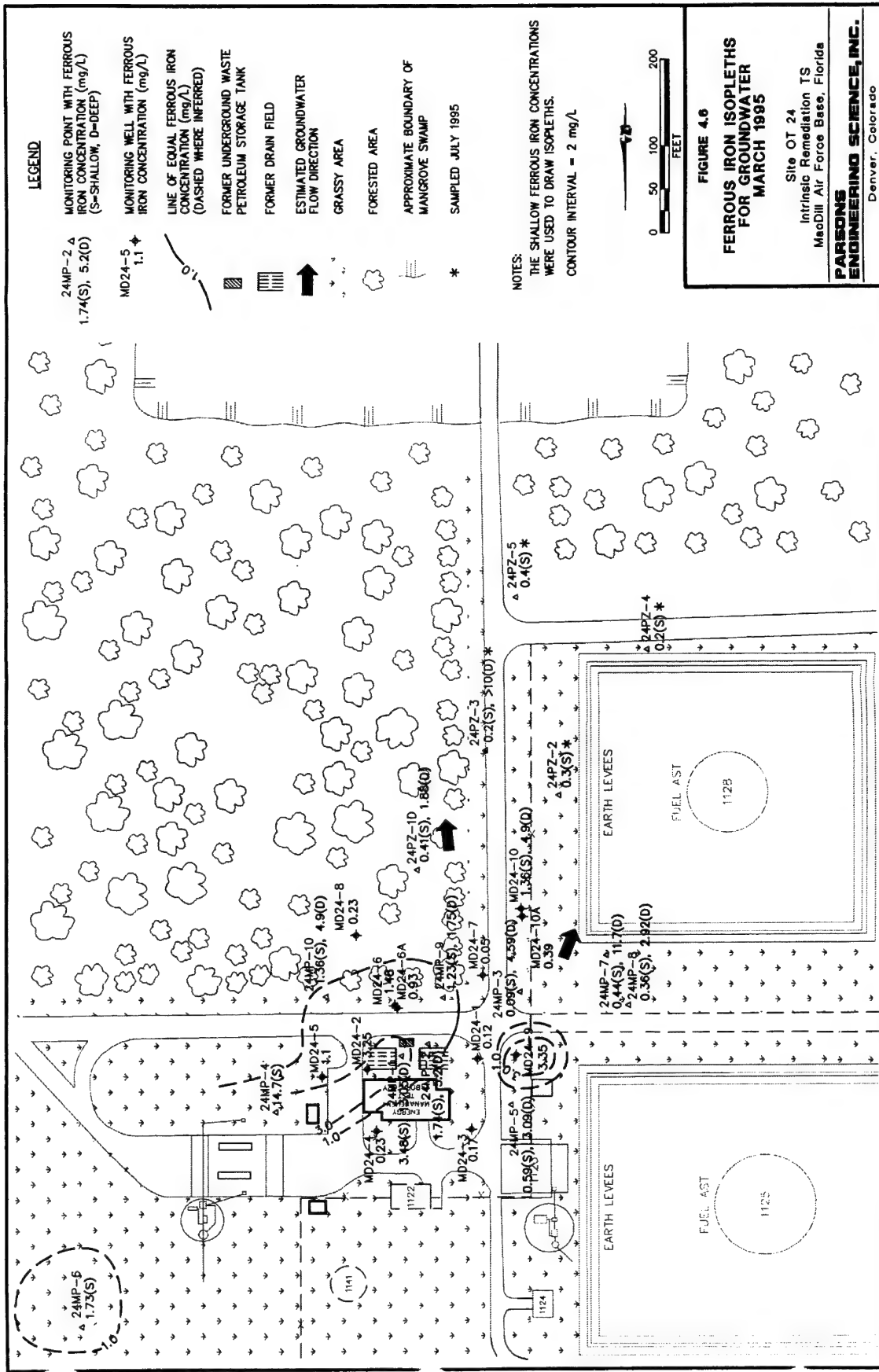
Although this process results in more efficient utilization of electron receptors, it is only applicable as the net cell mass of the microbial population continues to grow. Because groundwater contamination has been present at Site OT 24 for a number of years, it is expected that biomass production within the center of the plume has reached steady state. Therefore, the cell mass reaction equations would no longer apply. However, the higher rates of BTEX degradation could still apply in the downgradient portions of the plume.

4.3.2.2 Nitrate/Nitrite

Concentrations of nitrate and nitrite were measured at groundwater monitoring wells and monitoring points in March 1995 (Table 4.7). Nitrite was not detected, and nitrate was detected only in deep monitoring wells MD24-6A and MD24-10A at concentrations of 2.46 and 1.09 mg/L, respectively. Therefore, nitrate and nitrite do not appear to be present in detectable concentrations in the shallow portion of the surficial aquifer, and consequently denitrification does not appear to be a significant biodegradation process at Site OT 24.

4.3.2.3 Ferrous Iron

Figure 4.6 is an isopleth map showing the distribution of ferrous iron in groundwater, and Table 4.7 summarizes ferrous iron concentrations. Comparison of Figures 4.4 and 4.6 suggests that ferrous iron is being produced in the area of the BTEX plume via the reduction of ferric iron during anaerobic biodegradation of BTEX compounds. Shallow ferrous iron concentrations detected within the area bounded by the 10-µg/L BTEX isopleth (Figure 4.4) range from 0.41 mg/L at monitoring point 24PZ-1S to 3.48 mg/L at 24MP-1S, which is where the maximum dissolved BTEX concentration was detected. The average ferrous iron concentration within the 10-µg/L BTEX isopleth is 1.71 mg/L. The relatively large ferrous iron detections at upgradient monitoring point 24MP-4S (14.7 mg/L) and crossgradient well MD24-9 (3.35 mg/L)



are anomalous. Background levels of ferrous iron, measured in wells that are outside of or on the margin of the BTEX plume (see the nine wells listed for DO in Section 4.3.2.1) ranged from 0.13 mg/L to 1.73 mg/L, and averaged 0.40 mg/L.

The stoichiometry of BTEX oxidation to carbon dioxide, ferrous iron, and water by ferric iron reduction through anaerobic microbial biodegradation is presented in Table 4.6. On average, 37.5 moles of ferric iron hydroxide are required to metabolize one mole of total BTEX. Conversely, an average of 37.5 moles of ferrous iron are produced for each mole of total BTEX consumed. On a mass basis, this translates to approximately 21.8 mg ferrous iron produced for each 1 mg of total BTEX metabolized.

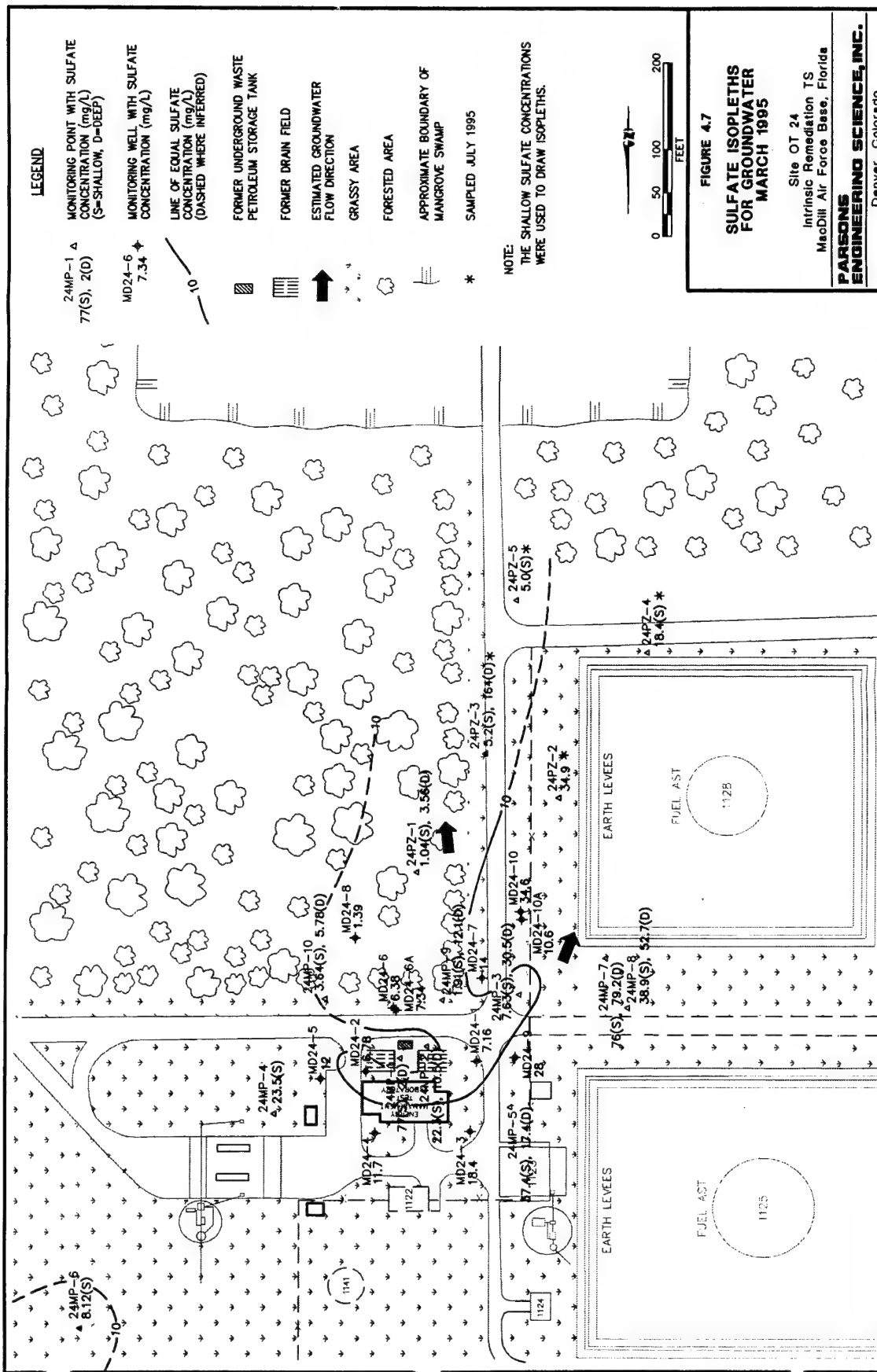
The highest measured Fe^{2+} concentration within the BTEX plume was 3.48 mg/L measured at monitoring point 24MP-1S. Assuming an average background ferrous iron concentration of 0.40 mg/L, this suggests that the shallow groundwater at this site has the capacity to assimilate 0.14 mg/L (140 $\mu\text{g/L}$) of total BTEX during iron reduction. This may be a conservative estimate of the assimilative capacity of iron because microbial cell mass production has not been taken into account by the stoichiometry shown in Table 4.6. In addition, this calculation is based on observed ferrous iron concentrations and not on the amount of ferric hydroxide available in the aquifer. Therefore, iron assimilative capacity could be much higher.

Recent evidence suggests that the reduction of ferric iron to ferrous iron cannot proceed at all without microbial mediation (Lovley and Phillips, 1988; Lovley *et al.*, 1991; Chapelle, 1993). None of the common organic compounds found in low-temperature, neutral, reducing groundwater could reduce ferric oxyhydroxides to ferrous iron under sterile laboratory conditions (Lovley *et al.*, 1991). This means that the reduction of ferric iron requires microbial mediation by microorganisms with the appropriate enzymatic capabilities. Because the reduction of ferric iron cannot proceed without microbial intervention, the elevated concentrations of ferrous iron that were measured in the contaminated groundwater at the site are very strong indicators of microbial activity.

4.3.2.4 Sulfate

Figure 4.7 is an isopleth map showing the distribution of sulfate in shallow groundwater in March 1995. Sulfate concentrations in shallow groundwater at the site ranged from 1.04 mg/L to 77 mg/L (Table 4.7). Comparison of Figures 4.4 and 4.7 shows graphically that areas with elevated total BTEX concentrations generally have depleted sulfate concentrations. This is a strong indication that anaerobic biodegradation of BTEX compounds is occurring at the site through the microbially mediated process of sulfate reduction. However, the highest sulfate concentration was detected in monitoring point 24MP-1S, which also had the highest dissolved BTEX concentration. This may be due to a relatively high sulfate concentration in the LNAPL that is inferred to be present in the vicinity of this monitoring point.

The stoichiometry of BTEX mineralization to carbon dioxide, sulfur, and water by sulfate reduction through anaerobic microbial biodegradation is presented in Table 4.6. The average mass ratio of sulfate to total BTEX is approximately 4.7 to 1. This



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translates to the mineralization of approximately 0.21 mg of total BTEX for every 1.0 mg of sulfate consumed.

Sulfate concentrations measured in 10 monitoring wells/points that are outside or on the margin of the dissolved BTEX plume (see the wells/points listed for DO in Section 4.3.2.1) ranged from 1.39 mg/L to 34.9 mg/L and averaged 15.0 mg/L. However, the distribution of shallow sulfate concentrations suggests that concentrations detected at monitoring wells/points MD24-5, MD24-4, MD24-3, MD24-10, 24PZ-2S, and 24PZ-4S are most representative of background sulfate concentrations. These concentrations ranged from 11.7 mg/L to 34.9 mg/L, and averaged 23.6 mg/L. Using this average concentration, the shallow groundwater at this site has the capacity to assimilate approximately 4.96 mg/L (4,960 µg/L) of total BTEX during sulfate reduction. This may be a conservative estimate of the assimilative capacity of sulfate in the groundwater because microbial cell mass production has not been taken into account by the stoichiometry presented in Table 4.6.

4.3.2.5 Methane

Figure 4.8 is an isopleth map showing the distribution of methane in groundwater. Comparison of Figures 4.4 and 4.8 shows graphically that areas with elevated total BTEX concentrations correlate with elevated methane concentrations. This is a strong indication that anaerobic biodegradation of the BTEX compounds by methanogenesis is occurring at the site.

Methane concentrations detected in shallow groundwater ranged from 0.008 mg/L to 9.89 mg/L, with the highest concentration detected in monitoring point 24MP-2S, located immediately south of the EMTL near the area of maximum dissolved BTEX concentrations (Table 4.7). Background levels of methane at 10 monitoring wells/points outside of or on the margin of the BTEX plume (see the wells/points listed for DO in Section 4.3.2.1) ranged from 0.008 mg/L to 1.05 mg/L, and averaged 0.33 mg/L. Samples collected from monitoring wells and monitoring points located near the areas with the highest BTEX concentrations contain the highest methane concentrations. At six shallow wells/points located within the 10-µg/L BTEX isopleth (Figure 4.4) (24MP-1S, 24MP-2S, MD24-2, MD24-6, 24MP-10S, and 24PZ-1S), methane concentrations ranged from 0.70 to 9.89 mg/L and averaged 3.49 mg/L.

The stoichiometry of BTEX oxidation to carbon dioxide and methane by methanogenesis is presented in Table 4.6. On average, approximately 1 mg of total BTEX is mineralized for every 0.78 mg of methane produced. Given a maximum detected methane concentration of 9.89 mg/L and an assumed background concentration of 0.33 mg/L, the shallow groundwater has the capacity to assimilate approximately 12.3 mg/L (12,300 µg/L) of total BTEX through methanogenesis. This may be a conservative estimate of the assimilative capacity due to methanogenesis because microbial cell mass production was not taken into account by the stoichiometry shown in Table 4.6. In addition, these calculations are based on observed methane concentrations and not on the amount of carbon dioxide available in the aquifer. Because methanogenesis produces more carbon dioxide than it consumes, an unlimited supply of carbon dioxide is theoretically available once the process of methanogenesis has been initiated. Therefore, methanogenic assimilative capacity could be much higher.

4.3.2.6 Reduction/Oxidation Potential

Redox potentials were measured at groundwater monitoring wells/points in March 1995 (Table 4.7). Redox potential is a measure of the relative tendency of a solution to accept or transfer electrons. The redox potential of a groundwater system depends on which electron acceptors are being reduced by microbes during BTEX oxidation. The redox potential in shallow groundwater at Site OT 24 in March 1995 ranged from -238.3 millivolts (mV) at monitoring point 24MP-3S to -18.7 mV at well MD24-4 (Figure 4.9). The preponderance of low measurements indicates that the groundwater in the shallow aquifer is generally reducing. This is consistent with the electron acceptor data, which indicate that the groundwater system beneath the study site has moved through the progression of redox reactions indicated on Table 4.6. Although the isopleths shown on Figure 4.9 suggest a general tendency for the lowest redox potentials to occur within and along the flowpath of the BTEX plume, there are no readily apparent trends. For example, redox potentials measured in six monitoring wells/points located outside of or on the margins of the BTEX plume (24MP-6S, MD24-5, MD24-8, MD24-4, MD24-3, and MD24-10) averaged -118 mV. This redox potential is very similar to the average potential of -126 mV measured in six wells/points within the 10- μ g/L dissolved BTEX isopleth (Figure 4.4).

4.3.2.7 Alkalinity

Total alkalinity (as calcium carbonate) was measured at groundwater monitoring wells/points in March 1995 (Table 4.7). Alkalinity is a measure of the ability of water to buffer changes in pH caused by the addition of biologically generated acids. In general, as the amount of total dissolved BTEX that is being oxidized increases, the total alkalinity increases. This is expected because the microbially-mediated reactions causing biodegradation of fuel hydrocarbons produce carbon dioxide (Table 4.8). Changes in alkalinity are most pronounced during aerobic respiration, denitrification, iron reduction, and sulfate reduction and less pronounced during methanogenesis (Morel and Hering, 1993). In addition, Willey *et al.*, (1975) show that short-chain aliphatic acid ions, which can be produced during biodegradation of fuel hydrocarbons as intermediates, can contribute to alkalinity in groundwater.

Total alkalinity in shallow groundwater at Site 57 is in the moderate range for groundwater, varying from 200 mg/L at monitoring point 24MP-2S to 620 mg/L at 24MP-4S. The highest alkalinity value was detected at monitoring point 24MP-4S, which is located east of the EMTL. Alkalinity values in six monitoring wells/points located within the 10- μ g/L BTEX isopleth (Figure 4.4) (24MP-1S, 24MP-2S, 24MP-10S, MD24-2, MD24-6, and 24PZ-1D) ranged from 200 mg/L to 460 mg/L and averaged 323 mg/L. This level of alkalinity should be sufficient to completely buffer potential changes in pH caused by biologically mediated BTEX oxidation reactions. Alkalinity values detected in six monitoring wells/points located outside of or on the margin of the BTEX plume (24MP-6S, MD24-5, MD24-3, MD24-4, MD24-10, and MD24-8) ranged from 240 to 400 mg/L and averaged 307 mg/L. The similarity in alkalinity values within and outside of the BTEX plume indicates that the biodegradation processes operating at the site are not significantly increasing the alkalinity of the groundwater. This observation supports the predominance of methanogenesis as a biodegradation mechanism at Site OT 24, which does not cause significant changes in alkalinity.

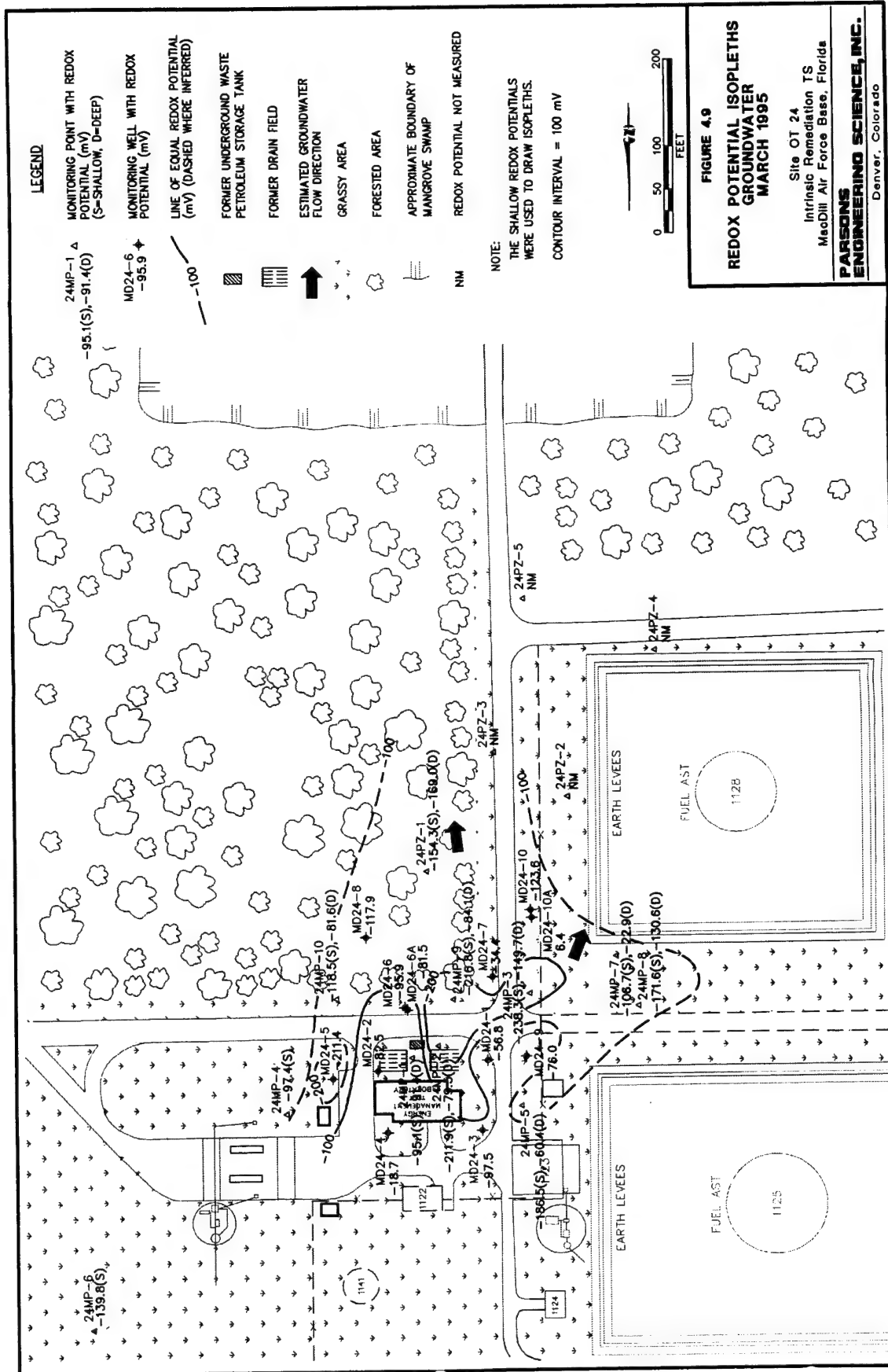


TABLE 4.8
MASS RATIO OF ALKALINITY (AS CaCO_3) PRODUCED TO BTEX
DEGRADED DURING AEROBIC RESPIRATION, DENITRIFICATION,
IRON (III) REDUCTION, AND SULFATE REDUCTION
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Alkalinity Production Reaction	Stoichiometric Mass Ratio of Alkalinity Produced to BTEX Degraded	Mass of Compound Degraded (mg) per unit mass of Alkalinity Produced (mg)
$\text{C}_6\text{H}_6 \rightarrow 6\text{CO}_2 \rightarrow 6\text{CaCO}_3$ <i>Benzene Oxidation</i>	600:78	0.13
$\text{C}_7\text{H}_8 \rightarrow 7\text{CO}_2 \rightarrow 7\text{CaCO}_3$ <i>Toluene Oxidation</i>	700:92	0.13
$\text{C}_8\text{H}_{10} \rightarrow 8\text{CO}_2 \rightarrow 8\text{CaCO}_3$ <i>Ethylbenzene Oxidation</i>	800:104	0.13
$\text{C}_8\text{H}_{10} \rightarrow 8\text{CO}_2 \rightarrow 8\text{CaCO}_3$ <i>Xylene Oxidation</i>	800:104	0.13

4.3.2.8 pH

Measurements of groundwater pH made in March 1995 are summarized in Table 4.7. Measured pH values ranged from 5.61 to 7.66 standard units; all but one of the values are within the optimal pH range of 6 to 8 for BTEX-degrading microbes in groundwater. Denitrification and methanogenic biodegradation rates are usually optimum between pH 7 and 8, and may drop off rapidly (but not cease altogether) below pH 6.

4.3.2.9 Temperature

Groundwater temperature measurements made in March 1995 are summarized in Table 4.7. Temperature affects the types and growth rates of bacteria that can be supported in the groundwater environment, with high temperatures generally resulting in higher growth rates. Temperatures in the shallow aquifer varied from 20.6 degrees Celsius ($^{\circ}\text{C}$) to 30.0 $^{\circ}\text{C}$. These are relatively warm temperatures for shallow groundwater, suggesting that bacterial growth rates should be enhanced.

4.3.2.10 Expressed Assimilative Capacity

The data presented in the preceding sections suggest that mineralization of BTEX compounds is occurring primarily through the microbially mediated processes of sulfate reduction and methanogenesis. Based on the stoichiometry presented in Table 4.6, the expressed BTEX assimilative capacity of groundwater at Site OT 24 is at least 17,500 $\mu\text{g/L}$ (Table 4.9).

A closed system with 2 liters of water can be used to help visualize the physical meaning of assimilative capacity. Assume that the first liter contains no fuel hydrocarbons, but it contains fuel degrading microorganisms and has an assimilative capacity of exactly "x" μg of fuel hydrocarbons. The second liter has no assimilative capacity; however, it contains fuel hydrocarbons. As long as these 2 liters of water are kept separate, biodegradation of the fuel hydrocarbons will not occur. If these 2 liters are combined in a closed system, biodegradation will commence and continue until the fuel hydrocarbons are depleted, the electron acceptors are depleted, or the environment becomes acutely toxic to the fuel-degrading microorganisms. Assuming a nonlethal environment, if fewer than "x" μg of fuel hydrocarbons were in the second liter, all of the fuel hydrocarbons will eventually degrade given a sufficient time; likewise, if greater than "x" μg of fuel hydrocarbons were in the second liter of water, only "x" μg of fuel hydrocarbons would ultimately degrade.

The groundwater beneath Site OT 24 is an open system, which continually receives additional electron receptors from upgradient flow and the infiltration of precipitation. This means that the assimilative capacity is not a fixed entity as it is in a closed system, and therefore cannot be compared directly to contaminant concentration in the groundwater. Rather, the expressed assimilative capacity of groundwater is intended to serve as a qualitative tool. Although the expressed assimilative capacity at this site is greater than the highest measured total BTEX concentration, the fate of BTEX in groundwater and the potential impact to receptors is dependent on the relationship between the kinetics of biodegradation and the solute transport velocity (Chapelle, 1994). This significant expressed assimilative capacity is a strong indicator that

TABLE 4.9
EXPRESSED ASSIMILATIVE CAPACITY OF SITE GROUNDWATER
SITE 0T 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Electron Acceptor or Process	Expressed BTEX Assimilative Capacity (µg/L)
Dissolved Oxygen	100
Nitrate	0
Iron Reduction	140
Sulfate	4,960
Methanogenesis	12,300
Expressed Assimilative Capacity	17,500

biodegradation is occurring; however, it is not confirmation that biodegradation will proceed to completion before potential downgradient receptors are impacted.

4.3.3 Processes of Intrinsic Remediation for Chlorinated Solvents

Although the focus of this demonstration was on intrinsic remediation of the BTEX compounds, the fate and transport of the chlorinated solvents in the groundwater must be considered when determining the type of remedial action warranted at the site. The following paragraphs describe biodegradation mechanisms for chlorinated solvents, and the evidence supporting the occurrence of chlorinated solvent biodegradation in Site OT 24 groundwater.

4.3.3.1 Electron Acceptor Reactions (Reductive Dehalogenation)

Under anaerobic conditions, biodegradation of chlorinated solvents usually proceeds through a process called reductive dehalogenation. During this process, the halogenated hydrocarbon is used as an electron acceptor, not as a source of carbon, and a halogen atom is removed and replaced with a hydrogen atom. Figure 4.10 illustrates the transformation of chlorinated ethenes via reductive dehalogenation. In general, reductive dehalogenation occurs by sequential dehalogenation from PCE to TCE to DCE to VC to ethene. Depending upon environmental conditions, this sequence may be interrupted, with other processes then acting upon the products. During reductive dehalogenation, all three isomers of DCE can theoretically be produced; however, Bouwer (1994) reports that under the influence of biodegradation, *cis*-1,2-DCE is a more common intermediate than *trans*-1,2-DCE, and that 1,1-DCE is the least prevalent intermediate of the three DCE isomers. Reductive dehalogenation of chlorinated solvent compounds is associated with the accumulation of daughter products and an increase in chloride.

Reductive dehalogenation affects each of the chlorinated ethenes differently. Of these compounds, PCE is the most susceptible to reductive dehalogenation because it is the most oxidized. Conversely, VC is the least susceptible to reductive dehalogenation because it is the least oxidized of these compounds. The rate of reductive dehalogenation also has been observed to decrease as the degree of chlorination decreases (Vogel and McCarty, 1985; Bouwer, 1994). Murray and Richardson (1993) have postulated that this rate decrease may explain the accumulation of VC in PCE and TCE plumes that are undergoing reductive dehalogenation.

In addition to being affected by the degree of chlorination of the CAH, reductive dehalogenation can also be controlled by the redox conditions of the site groundwater system. In general, reductive dehalogenation has been demonstrated under anaerobic nitrate-, ferric iron-, and sulfate-reducing conditions, but the most rapid biodegradation rates, affecting the widest range of CAHs, occur under methanogenic conditions (Bouwer, 1994). Dehalogenation of PCE and TCE to DCE can proceed under mildly reducing conditions such as nitrate reduction or iron (III) reduction (Vogel *et al.*, 1987), while the transformation of DCE to VC, or the transformation from VC to ethene requires more strongly reducing conditions (Freedman and Gossett, 1989; DeStefano *et al.*, 1991).

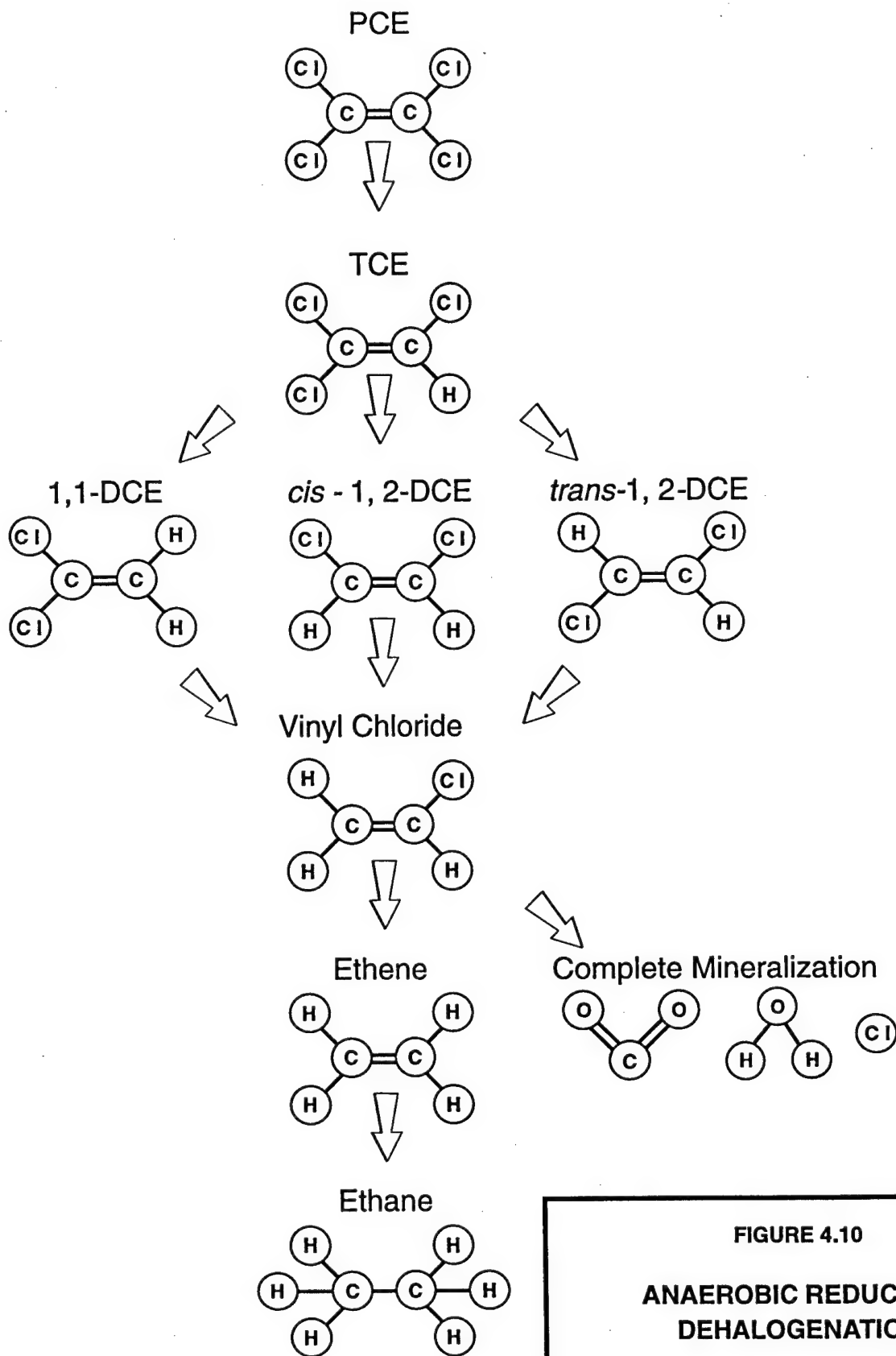


FIGURE 4.10

**ANAEROBIC REDUCTIVE
DEHALOGENATION**

Site OT 24
Intrinsic Remediation TS
MacDill Air Force Base, Florida

**PARSONS
ENGINEERING SCIENCE, INC.**

Because CAH compounds are used as electron acceptors, there must be an appropriate source of carbon for microbial growth in order for reductive dehalogenation to occur (Bouwer, 1994). Potential carbon sources can include low-molecular-weight compounds (e.g., lactate, acetate, methanol, or glucose) present in natural organic matter, or fuel hydrocarbons.

4.3.3.2 Electron Donor Reactions

Under aerobic conditions some CAH compounds can be utilized as the primary substrate (i.e., electron donor) in biologically mediated redox reactions (McCarty and Semprini, 1994). In this type of reaction, the facilitating microorganism obtains energy and organic carbon from the degraded CAH. In contrast to reactions in which the CAH is used as an electron acceptor, only the least oxidized CAHs (e.g., VC, DCE, or chlorobenzene) may be utilized as electron donors in biologically mediated redox reactions.

For example, while Murray and Richardson (1993) write that microorganisms are generally believed to be incapable of growth using TCE and PCE, other less chlorinated CAHs have been shown to be used as substrates. Davis and Carpenter (1990) describe the aerobic oxidation of VC in groundwater. McCarty and Semprini (1994) describe investigations in which VC and 1,2-DCA were shown to serve as primary substrates. These authors also document that dichloromethane has the potential to function as a primary substrate under either aerobic or anaerobic environments. Klier *et al.* (1996) describe aerobic mineralization of all three isomers of DCE. In addition, Bradley and Chapelle (1996) show evidence of oxidation of VC under iron-reducing conditions so long as there is sufficient bioavailable iron (III). Aerobic metabolism of VC may be characterized by a loss of VC mass, a decreasing molar ratio of VC to other CAH compounds, and the presence of chloromethane.

4.3.3.3 Cometabolism

When a CAH is biodegraded through cometabolism, it serves as neither an electron acceptor nor a primary substrate in a biologically mediated redox reaction. Instead, the degradation of the CAH is catalyzed by an enzyme or cofactor that is fortuitously produced by organisms for other purposes. The organism receives no known benefit from the degradation of the CAH; rather the cometabolic degradation of the CAH may in fact be harmful to the microorganism responsible for the production of the enzyme or cofactor (McCarty and Semprini, 1994).

Cometabolism is best documented in aerobic environments, although it potentially could occur under anaerobic conditions. Aerobic biodegradation pathways for chlorinated ethenes are illustrated in Figure 4.11. It has been reported that under aerobic conditions chlorinated ethenes, with the exception of PCE, are susceptible to cometabolic degradation (Murray and Richardson, 1993; Vogel, 1994; McCarty and Semprini, 1994). Vogel (1994) further elaborates that the cometabolism rate increases as the degree of dehalogenation decreases.

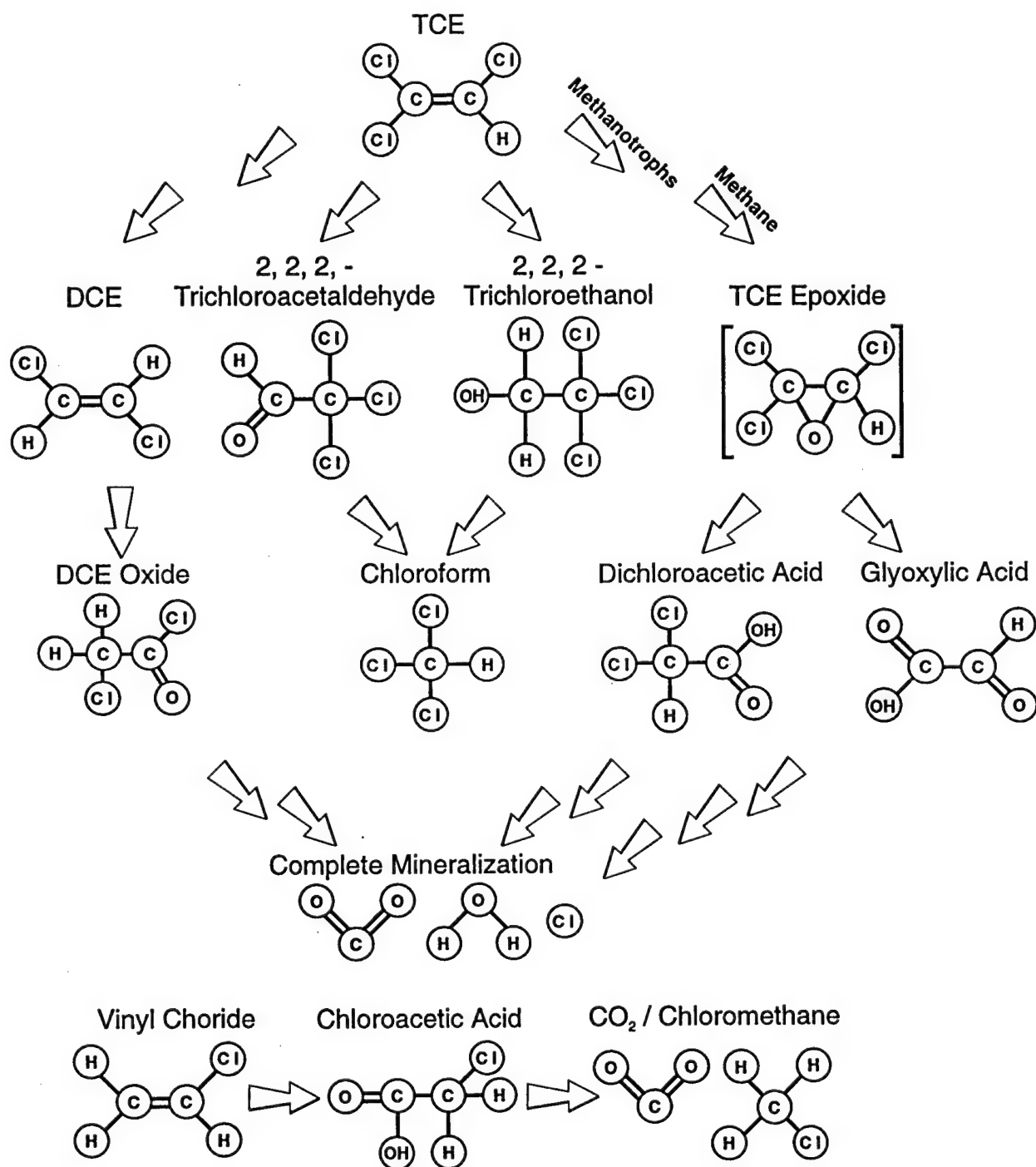


FIGURE 4.11

AEROBIC DEGRADATION

Site OT 24
Intrinsic Remediation TS
MacDill Air Force Base, Florida

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In the cometabolic process, TCE is indirectly transformed by bacteria as they use BTEX or another substrate to meet their energy requirements. Therefore, TCE does not enhance the degradation of BTEX or other carbon sources, nor will its cometabolism interfere with the use of electron acceptors involved in the oxidation of those carbon sources. It is likely that depletion of suitable substrates (BTEX or other organic carbon sources) may limit cometabolism of CAHs.

4.3.3.4 Biodegradation of Chlorinated Solvents at Site OT 24

The relative abundance of vinyl chloride in Site OT 24 groundwater (which is a daughter product produced as a result of the biodegradation of parent compounds such as PCE, TCE, and/or DCE), and the corresponding scarcity of potential parent compounds, indicates that biodegradation of CAHs is occurring by reductive dehalogenation, and that the majority of the parent compound(s) have been degraded. The occurrence of anaerobic vinyl chloride biodegradation by reductive dehalogenation in site groundwater is supported by the detection of ethene (a byproduct of vinyl chloride biodegradation) in the two samples containing the highest vinyl chloride concentrations (24MP-1S and MD24-6A). Ethene was not detected in the shallow well paired with MD24-6A (MD24-6), and the vinyl chloride concentration at this well was less than 1 µg/L. This may be due to the more rapid biodegradation of vinyl chloride in the relatively aerobic conditions that are more likely to sometimes prevail near the groundwater surface as a result of precipitation recharge. The anaerobic biodegradation (reductive dehalogenation) of vinyl chloride, which may be occurring at depth in the surficial aquifer, is less rapid and results in the production of ethene. The presence of *cis*-1,2-DCE as opposed to other DCE isomers also supports the occurrence of reductive dehalogenation. Bouwer (1994) reports that under the influence of biodegradation, *cis*-1,2-DCE is a more common intermediate than *trans*-1,2-DCE, and that 1,1-DCE is the least prevalent intermediate of the three DCE isomers. Manufactured DCE consists mostly of the *trans* isomer.

The vinyl chloride concentrations detected at monitoring point pair 24PZ-1S and 24PZ-1D were 2.8 µg/L and 1.0 µg/L, respectively. These low concentrations are similar to the Florida drinking water standard for this compound of 1 µg/L (FDER, 1989), and suggest that the vinyl chloride plume does not extend a substantial distance downgradient from these points.

SECTION 5

GROUNDWATER MODEL

5.1 GENERAL OVERVIEW AND MODEL DESCRIPTION

In order to help estimate degradation rates for dissolved BTEX compounds at Site OT 24 and to help predict the future migration of these compounds, Parsons ES modeled shallow groundwater flow and the fate and transport of the dissolved BTEX plume. The modeling effort had three primary objectives: 1) to predict the future extent and concentration of the dissolved contaminant plume by modeling the combined effects of advection, dispersion, sorption, and biodegradation; 2) to assess the potential for downgradient receptors to be exposed to contaminants at concentrations above regulatory levels of concern; and 3) to provide technical support for the natural attenuation remedial option at post-modeling regulatory negotiations. The model was developed using site-specific data and conservative assumptions about governing physical and chemical processes. Because of the conservative nature of model input, the reduction in contaminant mass caused by natural attenuation is expected to exceed model predictions. This analysis is not intended to represent a baseline assessment of potential risks posed by site contamination.

The Bioplume II code was used to estimate the potential for dissolved BTEX migration and degradation by natural mechanisms operating at Site OT 24. The Bioplume II model incorporates advection, dispersion, sorption, and biodegradation to simulate contaminant plume migration and degradation. The model is based upon the US Geological Survey (USGS) Method of Characteristics (MOC) two-dimensional (2-D) solute transport model of Konikow and Bredehoeft (1978). The model was modified by researchers at Rice University to include an aerobic biodegradation component that is activated by a superimposed DO plume. Incorporating the work of Borden and Bedient (1986), the model assumes a reaction between DO and BTEX that is instantaneous relative to the advective groundwater velocity. Bioplume II solves the USGS 2-D solute transport equation twice, once for hydrocarbon concentrations in the aquifer and once for a DO plume. The two plumes are combined using superposition at every particle move to simulate the instantaneous, biologically-mediated, reaction between hydrocarbons and oxygen.

In recent years it has become apparent that anaerobic processes such as denitrification, iron reduction, sulfate reduction, and methanogenesis can be important BTEX degradation mechanisms (Grbic'-Galic', 1990; Beller *et al.*, 1992; Edwards *et al.*, 1992; Edwards and Grbic'-Galic', 1992, Grbic'-Galic' and Vogel, 1987; Lovely *et al.*, 1989; Hutchins, 1991). Because there is evidence that anaerobic biodegradation processes are occurring at Site OT 24, these processes were accounted for during Bioplume II modeling using a first-order anaerobic decay coefficient. The following

subsections discuss in more detail the model setup, input parameters and assumptions, model calibration, and simulation results.

5.2 CONCEPTUAL MODEL DESIGN AND ASSUMPTIONS

Prior to developing a groundwater model, it is important to determine if sufficient data are available to provide a reasonable estimate of aquifer conditions. In addition, it is important to ensure that any limiting assumptions can be justified. The most important assumption made when using the Bioplume II model is that electron-acceptor-limited biodegradation is occurring at the site. The Bioplume II model assumes that the limiting factors for biodegradation are: 1) the presence of an indigenous, hydrocarbon-degrading microbial population, and 2) sufficient background electron acceptor concentrations. Data and information presented in Section 4 suggest that sulfate and carbon dioxide (methanogenesis) are being used as the primary electron acceptors for anaerobic biodegradation. The model assumes that DO is the only electron acceptor that reacts instantaneously with the BTEX plume. Anaerobic biodegradation of petroleum hydrocarbons was simulated using a first-order decay constant. Selection of this constant is discussed in Section 5.3.5.

On the basis of the data presented in Section 3, the surficial aquifer through which the dissolved BTEX is migrating was conceptualized and modeled as a shallow unconfined aquifer composed primarily of fine- to medium-grained sand (Figures 3.2 and 3.3). The use of a 2-D model is appropriate at this site because the surficial aquifer appears to be relatively homogenous, and groundwater quality data suggest that the dissolved BTEX contamination has not migrated a significant distance vertically. Lithologic data obtained during borehole drilling (Section 3) suggest that this aquifer is bounded vertically by a clayey zone; the average saturated thickness of the surficial aquifer was estimated to be approximately 20 to 24 feet. Groundwater enters the site via underflow from the north to northeast, and, after migrating through the primary contaminant source area, migrates in a southerly to southwesterly direction beneath a densely forested area toward a mangrove swamp. Increased ET rates in the forested area relative to surrounding, less heavily vegetated areas, may depress the water table beneath the forest area and cause groundwater flow lines to bend toward this area.

Despite prior excavation of contaminated soil and limited recovery of mobile LNAPL, some mobile LNAPL appears to persist at least seasonally in the immediate vicinity of the former east drain field (Section 4.1.2). This LNAPL, as well as the associated residual soil contamination bordering the water table (smear zone), is a continuing source of dissolved BTEX that counteracts the beneficial effects of natural attenuation mechanisms. The infrastructure that was the source of historical fuel releases has been removed, and no additional fuel releases are expected at the site.

5.3 INITIAL MODEL SETUP

Where possible, the initial setup for this model was based on site-specific data. Where site-specific data were not available (e.g., effective porosity), reasonable assumptions were made on the basis of widely accepted literature values for materials similar to those found in the shallow aquifer. The following sections describe the basic model setup. Those Bioplume II model parameters that were varied during model calibration are discussed in Section 5.4.

5.3.1 Grid Design and Boundary Conditions

The Bioplume II model used in this study was modified to allow the use of up to 50 columns and 100 rows. The dimension of each column and row can range from 0.1 to 999.9 feet. A 23- by 37-cell grid was used to model Site OT 24. Each grid cell was 25 feet wide by 40 feet long. The grid was oriented with the longest dimension parallel to the overall direction of groundwater flow and dissolved BTEX migration. The model grid covers an area of 851,000 square feet, or approximately 19.5 acres. The full extent of the model grid is indicated on Figure 5.1. As shown on this figure, the model does not fully include the minor dissolved BTEX contamination detected in the vicinity of monitoring points 24MP-7 and 24MP-8. However, this contamination is insignificant relative to the much higher BTEX concentrations present immediately south of the EMTL.

Model boundaries are mathematical statements that represent hydrogeologic boundaries, such as areas of specified head (e.g., surface water bodies or contour lines of constant hydraulic head) or specified flux. Hydrogeologic boundaries are represented by three mathematical statements that describe the hydraulic head at the model boundaries. These include:

- Specified-head boundaries (Dirichlet condition) for which the head is determined as a function of location and time only. Surface water bodies exhibit constant-head conditions. Specified-head boundaries are expressed mathematically as:

$$\text{Head} = f(x, y, z, t)$$

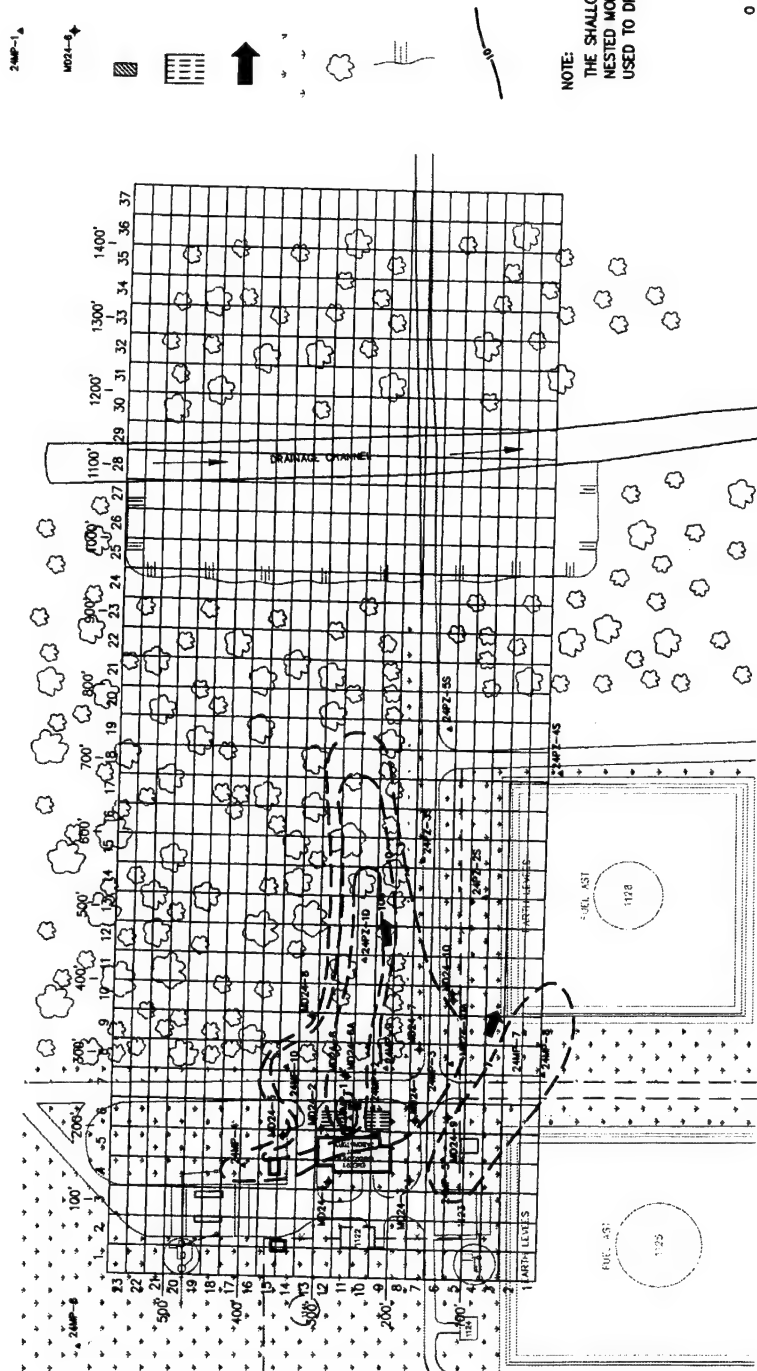
- Specified-flow boundaries (Neumann conditions) for which the mathematical description of the flux across the boundary is given. The flux is defined as a volumetric flow rate per unit area (e.g., $\text{ft}^3/\text{ft}^2/\text{day}$). No-flow boundaries are a special type of specified-flow boundary and are set by specifying the flux to be zero. Examples of no-flow boundaries include groundwater divides and impermeable hydrostratigraphic units. Specified-flux boundaries are expressed mathematically as:

$$\text{Flux} = f(x, y, z, t)$$

- Head-dependent flow boundaries (Cauchy or mixed-boundary conditions) where the flux across the boundary is calculated from a given boundary head value. This type of flow boundary is sometimes referred to as a mixed-boundary condition because it is a combination of a specified-head boundary and a specified-flow boundary. Head-dependent flow boundaries are used to model leakage across semipermeable boundaries. Head-dependent flow boundaries are expressed mathematically as (Bear, 1979):

$$\text{Flux} = \frac{(H_0 - H)K'}{B'}$$

- LEGEND**
- 24MP-1A
 - 24MP-2A
 - PARSONS ES MONITORING POINT
 - PRE-EXISTING MONITORING WELL
 - FORMER UNDERGROUND WASTE PETROLEUM STORAGE TANK
 - FORMER DRAIN FIELD
 - ESTIMATED GROUNDWATER FLOW DIRECTION
 - GRASSY AREA
 - FORESTED AREA
 - APPROXIMATE BOUNDARY OF MANGROVE SWAMP
 - LINE OF EQUAL BTEX CONCENTRATION ($\mu\text{g/L}$) (DASHED WHERE INFERRED)



NOTE:
THE SHALLOW BTEX CONCENTRATIONS FROM NESTED MONITORING POINTS/WELLS WERE USED TO DRAW ISOPLETHS.



FIGURE 5.1
MODEL GRID SUPERIMPOSED
ON DISSOLVED BTEX ISOPLETHS
MARCH 1995

Site OT 24
Intrinsic Remediation TS
Meadell Air Force Base, Florida

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where: H = Head in the zone being modeled (generally the zone containing the contaminant plume),
 H_0 = Head in external zone (separated from plume by semipermeable layer),
 K' = Hydraulic conductivity of semipermeable layer, and
 B' = Thickness of semipermeable layer.

Natural hydraulic boundaries are modeled using a combination of the three types of model boundary conditions listed above. When possible, hydrologic boundaries such as surface water bodies, groundwater divides, or hydrologic barriers should coincide with the perimeter of the model. In areas lacking obvious hydrologic boundaries, specified-head or specified-flux boundaries can be specified at the model perimeter if the boundaries are far enough removed from the contaminant plume that transport calculations are not affected. Bioplume II requires the entire model domain to be bounded by zero-flux cells (also known as no-flow cells), with other boundary conditions established within the subdomain specified by the no-flow cells.

Specified-head boundaries for the model were set on portions of the northern, eastern and western edges of the model grid in areas where the water table isopleths indicated that groundwater was either entering or leaving the model domain. These specified-head cells were used to simulate the groundwater flow and contaminant migration observed at the site. The east/west-trending drainage channel located approximately 900 feet south of the EMTL (Figure 5.1) was also designated a specified-head boundary. The hydraulic heads along the drainage channel were estimated to range from 1.85 to 1.80 feet msl. In reality, the northern edge of the mangrove swamp located north of the drainage channel may also constitute a specified-head boundary. However, the degree to which groundwater underflow in the surficial aquifer beneath the swamp occurs is not known; therefore, a boundary was not inserted in the model at this location. The specified heads along the western, northern, and eastern model boundaries ranged from 3.38 to 4.32 feet msl, 4.32 to 5.10 feet msl, and 3.90 to 5.10 feet msl, respectively. These constant-head cells were placed far enough away from the main BTEX plume to avoid potential boundary interferences.

The portions of the eastern and western model boundaries that were not configured as specified-head boundaries were designated as no-flow (specified flux) boundaries. In this case, the flux through these boundaries is assumed to be zero because flow is generally parallel to these boundaries. The base or lower boundary of the model is also assumed to be no-flow, and is defined by the upper surface of the confining clay layer (Figure 3.2). Shallow aquifer thicknesses of 15 to 25 feet were used in the model based on the stratigraphic information presented in Section 3. The upper model boundary is defined by the simulated water table surface.

5.3.2 Groundwater Elevation and Gradient

The October 1995 water table elevation map presented on Figure 3.6 was used to define the starting heads input into the Bioplume II model. The configuration of groundwater elevation isopleths on this figure indicates that groundwater flow in the

immediate vicinity of the EMTL at Site OT 24 is to the southwest. However, the distribution of dissolved BTEX concentrations (Figure 4.4) indicates a more southerly contaminant migration direction than is indicated by the water table isopleths, suggesting that the surficial aquifer may be anisotropic (i.e., the hydrogeologic properties vary with direction). In this case, the hydraulic conductivity in the north/south direction (parallel to the long axis of the model grid) may be greater than the hydraulic conductivity in the east/west direction. In the Bioplume model, the ratio of the longitudinal (north/south) to transverse (east/west) transmissivity was set at 1.1, introducing a slight degree of anisotropy. Additional groundwater flow direction and gradient data are presented by CH2M Hill (1990 and 1991a). These data are generally consistent with the data collected by Parsons ES in March, August, and October 1995. Therefore, it was assumed that the observed water levels were reasonably representative of steady-state conditions. As described in Section 5.4.1, the model was calibrated to the observed October 1995 water table.

5.3.3 BTEX Concentrations

Dissolved BTEX enters groundwater at Site OT 24 through two on-going processes: 1) contact between groundwater and mobile or residual LNAPL at or below the water table, and 2) migration of recharge (precipitation) through soil containing LNAPL above the water table. The suspected areal extent of both mobile and residual contamination is limited to the immediate vicinity of the former drain fields, UST, and oil/water separator (Figures 4.1 through 4.3). Partitioning of BTEX from these sources into groundwater was simulated using BTEX injection wells in the vicinity of the former drain fields. The methods used to estimate the leaching potential of both the mobile and residual LNAPL to groundwater are described in Section 5.4.2. The water injection rate for the injection well was set at a rate low enough that the hydraulic calibration of the model was not affected.

The total dissolved BTEX concentrations obtained from laboratory analytical results for each monitoring well/point location were used for model development. At well/point nests, the highest BTEX concentration observed at that location was used. Table 4.4 presents dissolved BTEX concentration data for March 1995, and Figure 4.4 shows the spatial distribution of dissolved BTEX compounds.

A comparison between the October 1990 (Appendix A) and March 1995 (Figure 4.4) BTEX plumes indicates substantial differences in both orientation and areal extent. The most apparent difference between the two plumes is that the 1990 plume is portrayed as being wholly confined to the immediate vicinity of the EMTL. This is probably due to the general lack of monitoring stations south of the EMTL in the forested area, and the resulting perception that the plume was migrating solely to the southwest. Another substantial difference between the plumes is the maximum BTEX concentrations detected in the source area. In October 1990, the maximum detected BTEX concentration was 42.5 µg/L, as opposed to a maximum detected concentration in 1995 of 2,840 µg/L. This difference can be attributed to the lack of monitoring wells in the heart of the source area in 1990, and the relatively deep screen depth of the nearest well. In 1990, the monitoring well nearest to the eastern drain field was MD24-2, which is located on the upgradient side of the drain field and screened between 10 and 20 feet bgs (Figure 5.1). Because the groundwater surface at this location is generally within 4 feet of the ground surface, and because the BTEX

compounds are generally most prevalent near the top of the surficial aquifer, the well screen is not positioned to detect maximum BTEX concentrations at this location. The shape and distribution of the BTEX plume is the result of advective-dispersive transport and biodegradation of dissolved BTEX contamination. As described in Section 5.4.2, the simulated BTEX plume was calibrated to resemble the observed BTEX plume in March 1995.

5.3.4 Dissolved Oxygen

As discussed previously, the Bioplume II model assumes an instantaneous reaction between the BTEX plume and the DO plume. The discussion presented in Section 4.3.2 suggests that sulfate and carbon dioxide (methanogenesis) are being used as primary electron acceptors for biodegradation of BTEX compounds at Site OT 24. The total BTEX plume at the site was modeled assuming that DO was the only electron acceptor being utilized at a rate that is instantaneous relative to the advective groundwater flow velocity for the biodegradation of the BTEX compounds. As described in Section 5.3.5, anaerobic biodegradation was accounted for through the use of a first-order decay rate constant.

Within the area characterized by elevated BTEX concentrations (greater than 10 $\mu\text{g/L}$), shallow DO concentrations measured in March 1995 ranged from 0.06 mg/L to 0.79 mg/L, increasing with distance to the south from the EMTL (see Section 4.3.2.1). The average (mean) DO concentration within the 10 $\mu\text{g/L}$ isopleth was 0.24 mg/L. DO concentrations in areas that are outside or on the margins of the BTEX plume ranged from 0.02 to 1.54 mg/L, and averaged 0.56 mg/L. The DO concentration measured at 24MP-5S (1.31 mg/L) was anomalously high and may be indicative of sample aeration or meter/probe malfunction. For model development, initial DO concentrations in the area surrounding the EMTL (model grid columns 1 through 10 and portions of column 11, Figure 5.1) were assumed to equal 0.10 mg/L, and the remaining model cells were assigned an initial DO concentration of 0.50 mg/L. In addition, it was assumed that background DO concentrations further upgradient from the site averaged 0.2 mg/L on the basis of measured DO concentrations in monitoring points 24MP-6 (0.11 mg/L) and 24MP-4 (0.3 mg/L). This assumption may be conservative considering the higher DO concentrations measured in shallow groundwater at and south of 24PZ-1D and the measured background DO concentration in very similar hydrogeologic conditions at Site 56, the Army Air Force Exchange Service (AAFES) service station at MacDill AFB, of 0.8 mg/L (Parsons ES, 1995b).

Due to the shallow water table and the presence of sandy soils with a relatively low natural organic carbon content (except in the forested area, where soils may have a higher natural organic carbon content), it is reasonable to assume that the precipitation that percolates through the vadose zone contains some DO when it reaches the water table. However, in areas where the soils are contaminated with petroleum, the recharge water may be substantially oxygen-depleted due to an abundance of oxygen-consuming microbial activity occurring in the contaminated interval. Assuming that the average temperature of precipitation falling on the site is 21°C (70 °F), the precipitation would have a DO concentration of approximately 8.7 mg/L. Some percentage of this DO is most likely consumed as the water percolates through the vadose zone as a result of microbial processes that utilize naturally occurring organic

carbon in the soil. To be conservative, DO was not added to the recharge water in this model.

5.3.5 Anaerobic Degradation Rates

Available data strongly suggest that anaerobic degradation is occurring at Site OT 24, and that aerobic degradation processes are relatively insignificant (Table 4.9). Anaerobic degradation must therefore be simulated with Bioplume II to make solute transport predictions that are meaningful. The Bioplume II model simulates anaerobic biodegradation by assuming that such degradation follows first-order kinetics. As with a large number of biological processes, anaerobic biodegradation can generally be described using a first-order rate constant and the equation:

$$\frac{C}{C_0} = e^{-kt}$$

where: C = Contaminant Concentration at Time t,
C₀ = Initial Contaminant Concentration,
k = Coefficient of Anaerobic Decay (anaerobic rate constant), and
t = time.

In order to calculate anaerobic rate constants, the apparent degradation rate must be normalized for the effects of dilution caused by advective/dispersive processes and groundwater recharge. This can be accomplished by normalizing the concentration of each contaminant to the concentration of a component of jet fuel (a tracer) that has sorptive properties similar to those of BTEX but that is fairly recalcitrant to biological degradation. Observed concentration data can be normalized to 1,3,5-trimethylbenzene (1,3,5-TMB), 1,2,4-TMB, 1,2,3-TMB, or 1,2,3,4-tetramethylbenzene (1,2,3,4-TEMB). The TMB compounds and TEMB can serve as good tracers because they can be relatively recalcitrant to biodegradation under anaerobic conditions, and they have sorptive properties similar to the BTEX compounds (Cozzarelli *et al.*, 1990 and 1994). The degree of biological recalcitrance of these tracer compounds is site-specific, and their use as conservative tracers must be evaluated on a case-by-case basis.

Alternatively, Buscheck and Alcantar (1995) derived a relationship that allows calculation of first-order decay rate constants for steady-state plumes. This method involves coupling the regression of contaminant concentration (plotted on a logarithmic scale) versus distance downgradient (plotted on a linear scale) to an analytical solution for one-dimensional, steady-state, contaminant transport that includes advection, dispersion, sorption, and biodegradation.

Analysis results for TMB and TEMB compounds (Table 4.4) indicated substantial reductions in the concentrations of these compounds with increasing distance from the source area along the plume flowpath. Therefore, these compounds do not appear to be biologically recalcitrant in the groundwater system beneath the site, and these data were

not used to compute decay rate constants. Decay rate constants ranging from 0.00037 day^{-1} to 0.00096 day^{-1} were calculated using the method of Buscheck and Alcantar (1995). The minimum calculated value of 0.00037 day^{-1} was calculated using an estimated average migration velocity for BTEX (the average computed retardation coefficient for BTEX was used). The maximum value of 0.00096 day^{-1} was calculated using an estimated average migration velocity for benzene, which appears to be the primary BTEX compound of concern in the downgradient portion of the plume (the BTEX detected at downgradient monitoring point 24PZ-1S consisted entirely of benzene). Rate constant calculations are contained in Appendix D. It is not known whether the dissolved BTEX plume at Site OT 24 is at steady-state. It is reasonable to conclude that steady-state conditions may have been present in 1989, when fuel releases to the subsurface ceased, because releases had been occurring for approximately 40 years, and the plume would have had ample time to reach steady state. Since fuel releases ceased (1989) and the source area was excavated (1991), some remission of the plume may have occurred.

During the calibration process, an intermediate value of 0.0007 day^{-1} was selected for use as the anaerobic decay coefficient in the model. Use of an intermediate value as opposed to the most conservative (lowest) value aided the calibration by narrowing the simulated BTEX plume and improving the match between the simulated and measured BTEX concentrations at downgradient monitoring point 24PZ-1S. The selected value is lower than decay constants frequently reported in the literature (Table 5.1), and is potentially conservative. For example, Chapelle (1994) reported that at two different sites with anaerobic conditions, the anaerobic decay rate constants both were approximately 0.01 day^{-1} . Wilson *et al.* (1994) report first-order anaerobic biodegradation rates of 0.007 to 0.185 day^{-1} . Stauffer *et al.* (1994) report rate constants of 0.01 and 0.018 day^{-1} for benzene and p-xylene, respectively. The selected anaerobic decay rate also is less than the rates computed for Site 56 at MacDill AFB (0.003 day^{-1}) (Parsons ES, 1995b) and for a site having similar hydrogeologic conditions at Eglin AFB in Florida (0.009 day^{-1}) (Parsons ES, 1995d). A similar rate (0.0005 day^{-1}) was used for modeling BTEX plume migration at the Pumphouse 75 site at MacDill AFB (Parsons ES, 1995c).

It should be noted that comparison of anaerobic decay rate coefficients with reported values from other sites is most valid if the site geochemical (e.g., redox and pH) conditions are similar. Negative redox values (measured at Site OT 24, indicating reducing conditions) also were measured at Site 56, the Eglin AFB site, and the Hill AFB, Utah site described in Wiedemeier *et al.*, (1995), and each of these sites contained sandy soils. The pH values at Site 56, Eglin AFB, and Hill AFB ranged from 6.2 to 7.3, 5.6 to 6.7, and 6.3 to 8.3, respectively. Measured pH values at Site OT 24 ranged from 5.6 to 7.7. Geochemical conditions for the remaining studies listed in Table 5.1 were not specified in the referenced documents.

5.4 MODEL CALIBRATION

Model calibration is an important component in the development of any numerical groundwater model. Calibration of the flow model demonstrates that the model is capable of matching hydraulic conditions observed at the site; calibration of a contaminant transport model superimposed upon the calibrated flow model helps verify that contaminant loading and transport conditions are being appropriately simulated.

TABLE 5.1
REPRESENTATIVE FIRST-ORDER ANAEROBIC DECAY RATE CONSTANTS
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Reference	Decay Rate (day ⁻¹)
Chapelle (1994)	0.01 ^{a/}
Buscheck <i>et al.</i> (1993)	0.001 to 0.01 ^{a/}
Wiedemeier <i>et al.</i> (1995b)	0.01 to 0.03 ^{a/}
Wiedemeier <i>et al.</i> (1995b)	0.03 to 0.04 ^{b/}
Wiedemeier <i>et al.</i> (1995b)	0.02 to 0.04 ^{c/}
Wiedemeier <i>et al.</i> (1995b)	0.01 to 0.03 ^{d/}
Wiedemeier <i>et al.</i> (1995b)	0.006 to 0.03 ^{e/}
Stauffer <i>et al.</i> (1994)	0.01 ^{b/} to 0.02 ^{e/}
MacIntyre <i>et al.</i> (1993)	0.01 to 0.02 ^{e/}
MacIntyre <i>et al.</i> (1993)	0.007 to 0.012 ^{b/}
MacIntyre <i>et al.</i> (1993)	0.006 to 0.012 ^{f/}
Barker <i>et al.</i> (1987)	0.007 ^{b/}
Kemblowski <i>et al.</i> (1987)	0.0085 ^{b/}
Chiang <i>et al.</i> (1989)	0.095 ^{b/}
Wilson <i>et al.</i> (1990)	0.007 to 0.024 ^{b/}
Howard <i>et al.</i> (1991)	0.009 to 0.069 ^{b/}

a/ For total BTEX.

b/ For benzene.

c/ For toluene.

d/ For ethylbenzene.

e/ For xylene.

f/ For naphthalene.

The numerical flow model presented herein was calibrated by altering transmissivity and recharge in a trial-and-error fashion until simulated heads approximated observed field values within a prescribed accuracy. After calibration of the flow model, the numerical solute transport model was calibrated by altering contaminant transport parameters and contaminant source term concentrations in a trial-and-error fashion until the simulated BTEX plume approximated observed field values. Table 5.2 lists input parameters used for the modeling effort. Model input and output are included in Appendix E.

5.4.1 Water Table Calibration

The shallow water table at Site OT 24 was assumed to be influenced by continuous recharge and discharge at the constant-head cells established at the upgradient and downgradient model boundaries. In addition, it was assumed that precipitation recharge entered the subsurface in the unpaved portions of the site. According to BVWS (1995), the average annual precipitation at the Base is approximately 44 inches per year, and the average annual ET rate is 39 inches per year (89 percent of precipitation). The recharge rate for the calibrated groundwater flow model was 10 inches per year in the grass-covered areas. In the gravel-covered areas within the POL fuel storage tank berms, a recharge rate of 27 inches per year was used. This relatively high value was used to reflect the lack of vegetation in these areas, and to simulate the groundwater mounding that appears to be present immediately east of fuel tank 1128 (Figure 3.6). A net groundwater discharge of 20 inches per year was used in the densely forested area immediately south of the EMTL due to the abundance of vegetation and the indications that the groundwater surface beneath this area is depressed (see Section 3.5). The forested area north of the mangrove swamp is populated largely by Brazilian pepper, which is a species capable of sustaining relatively high ET rates. Similarly, ET rates in the mangrove swamp should be high due to the presence of standing water and the high ET capabilities of mangroves.

Hydraulic conductivity is an important aquifer characteristic that represents the ability of the water-bearing strata to transmit groundwater. Transmissivity is the product of the hydraulic conductivity and the thickness of the aquifer. An accurate estimate of hydraulic conductivity is important to help quantify advective groundwater flow velocities and to define the flushing potential of the aquifer and the quantity of electron-acceptor-charged groundwater that is entering the site from upgradient locations. According to Rifai *et al.* (1988), the Bioplume II model is particularly sensitive to variations in hydraulic conductivity. Lower values of hydraulic conductivity result in a slower-moving plume with a relatively small areal extent and higher average BTEX concentrations. Higher values of hydraulic conductivity result in a faster-moving plume that is spread over a larger area and contains lower average BTEX concentrations.

Saturated thickness data from previous reports, geologic logs, and water level measurements were used in conjunction with the average hydraulic conductivity and transmissivity as determined from slug tests, Hydrocone® tests, and a pumping test (CH2M Hill, 1990 and this field effort) to estimate an initial uniform transmissivity for the entire model domain. As stated in Section 3.5, hydraulic conductivities derived from slug tests performed in the shallow sandy aquifer at Site OT 24 ranged from less than one to 57 ft/day, and transmissivity values derived from a pumping test ranged

TABLE 5.2
BIOPLUME II MODEL INPUT PARAMETERS
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Parameter	Description	Model Runs			
		Calibrated Model Setup	OT 24A	OT 24B	OT 24C
NTIM	Maximum number of time steps in a pumping period	1	1	1	1
NPMP	Number of Pumping Periods	1	31	26	26
NX	Number of nodes in the X direction	23	23	23	23
NY	Number of nodes in the Y direction	37	37	37	37
NPMAX	Maximum number of Particles $NPMAX = (NX-2)(NY-2)(NPTPND) + (Ns^w)(NPTPND) + 250$	7,000	7,000	7,000	7,000
NPNT	Time step interval for printing data	1	1	1	1
NITP	Number of iteration parameters	7	7	7	7
NUMOBS	Number of observation points	0	0	0	0
ITMAX	Maximum allowable number of iterations in ADIP ^w	200	200	200	200
NREC	Number of pumping or injection wells	6	6	6	7
NPTPND	Initial number of particles per node	9	9	9	9
NCODES	Number of node identification codes	3	3	3	3
NPNTMV	Particle movement interval (IMOV)	0	0	0	0
NPNTVL	Option for printing computed velocities	1	1	1	1
NPNTD	Option to print computed dispersion equation coefficients	0	0	0	0
NPDELC	Option to print computed changes in concentration	0	0	0	0
NPNCHV	Option to punch velocity data	0	0	0	0
NREACT	Option for biodegradation, retardation and decay	1	1	1	1
PINT	Pumping period (years)	42	/	/	/
TOL	Convergence criteria in ADIP	0.001	0.001	0.001	0.001
POROS	Effective porosity	0.25	0.25	0.25	0.25
BETA	Characteristic length (long. dispersivity; feet)	30	30	30	30

TABLE 5.2 (Continued)
BIOPLUME II MODEL INPUT PARAMETERS
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Parameter	Description	Model Runs			
		Calibrated Model Setup	OT 24A	OT 24B	OT 24C
S	Storage Coefficient	0 (Steady-State)	0	0	0
TIMX	Time increment multiplier for transient flow	-	-	-	-
TINIT	Size of initial time step (seconds)	-	-	-	-
XDEL	Width of finite difference cell in the x direction (feet)	25	25	25	25
YDEL	Width of finite difference cell in the y direction (feet)	40	40	40	40
DLTRAT	Ratio of transverse to longitudinal dispersivity	0.05	0.05	0.05	0.05
CELDIS	Maximum cell distance per particle move	0.5	0.5	0.5	0.5
ANFCTR	Ratio of Tyy to Txx (1 = isotropic)	1.1	1.1	1.1	1.1
DK	Distribution coefficient	0.312	0.312	0.312	0.312
RHOB	Bulk density of the solid (grams/cubic centimeter)	1.6	1.6	1.6	1.6
THALF	Half-life of the solute	-	-	-	-
DEC1	Anaerobic decay coefficient (day ⁻¹)	0.0007	0.0007	0.0007	0.0007
DEC2	Reaeration coefficient (day ⁻¹)	0	0	0	0
F	Stoichiometric Ratio of Hydrocarbons to Oxygen	3.0	3.0	3.0	3.0

a/ Ns - Number of nodes that represent fluid sources (wells or constant-head cells).

b/ ADIP = Alternating-direction implicit procedure (subroutine for solving groundwater flow equation).

c/ Duration of first pumping period was 42 years (calendar years 1953 - 1995); subsequent pumping periods each lasted 1 year.

from 98 to 223 square foot per day (ft²/day). Assuming an average aquifer thickness of 20 to 24 feet, these transmissivity values translate into hydraulic conductivity values ranging from 4 to 11 ft/day. To better match heads in the model to observed values measured in August 1996, the transmissivities were progressively varied in blocks and rows until the simulated water levels for cells corresponding to the selected well locations matched the observed water levels to an acceptable degree. Figure 5.2 shows the calibrated water table. Calibrated model hydraulic conductivities ranged between 5 and 27 ft/day, with the majority of conductivities ranging between 5 and 23 ft/day. Simulated advective velocities were variable, but generally ranged from 0.1 ft/day to 0.2 ft/day (36 to 72 feet per year along the plume migration corridor). These velocities are equal to slightly higher than the average velocity of 0.1 ft/day (36 feet per year) estimated prior to the start of the modeling using available hydraulic conductivity and hydraulic gradient data (see Section 3.5).

Water level elevation data from 16 monitoring well/point locations were used to compare measured and simulated heads for calibration. The 16 selected locations were MD24-1, MD24-2, MD24-3, MD24-4, MD24-5, MD24-6, MD24-7, MD24-9, MD24-10, 24PZ-1S, 24PZ-2S, 24PZ-3S, 24PZ-5S, 24MP-2S, 24MP-4S, and 24MP-5S.

The root mean squared (RMS) error is commonly used to express the average difference between simulated and measured heads. RMS error is the average of the squared differences between measured and simulated heads, and can be expressed as:

$$\text{RMS} = \left[\frac{1}{n} \sum_{i=1}^n (h_m - h_s)_i^2 \right]^{0.5}$$

where:

n = the number of points where heads are being compared,

h_m = measured head value, and

h_s = simulated head value.

The RMS error between observed and calibrated values at the 16 comparison points was 0.097 foot, which corresponds to a calibration error of 5.4 percent (water levels dropped approximately 1.8 feet over the portion of the model domain containing the monitoring wells/points listed above). RMS error calculations are summarized in Appendix D.

In solving the groundwater flow equation, Bioplume II establishes the water table surface and calculates an overall hydraulic balance that accounts for the numerical difference between flux into and out of the system. The hydraulic mass balance for the calibrated model was adequate to accomplish the objectives of this modeling effort, with 99.5 percent of the water flux into and out of the system being numerically accounted for (i.e., a 0.5-percent error). According to Anderson and Woessner (1992), a mass balance error of around 1 percent is acceptable, while Konikow (1978) indicates an error of less than 0.1 percent is ideal.

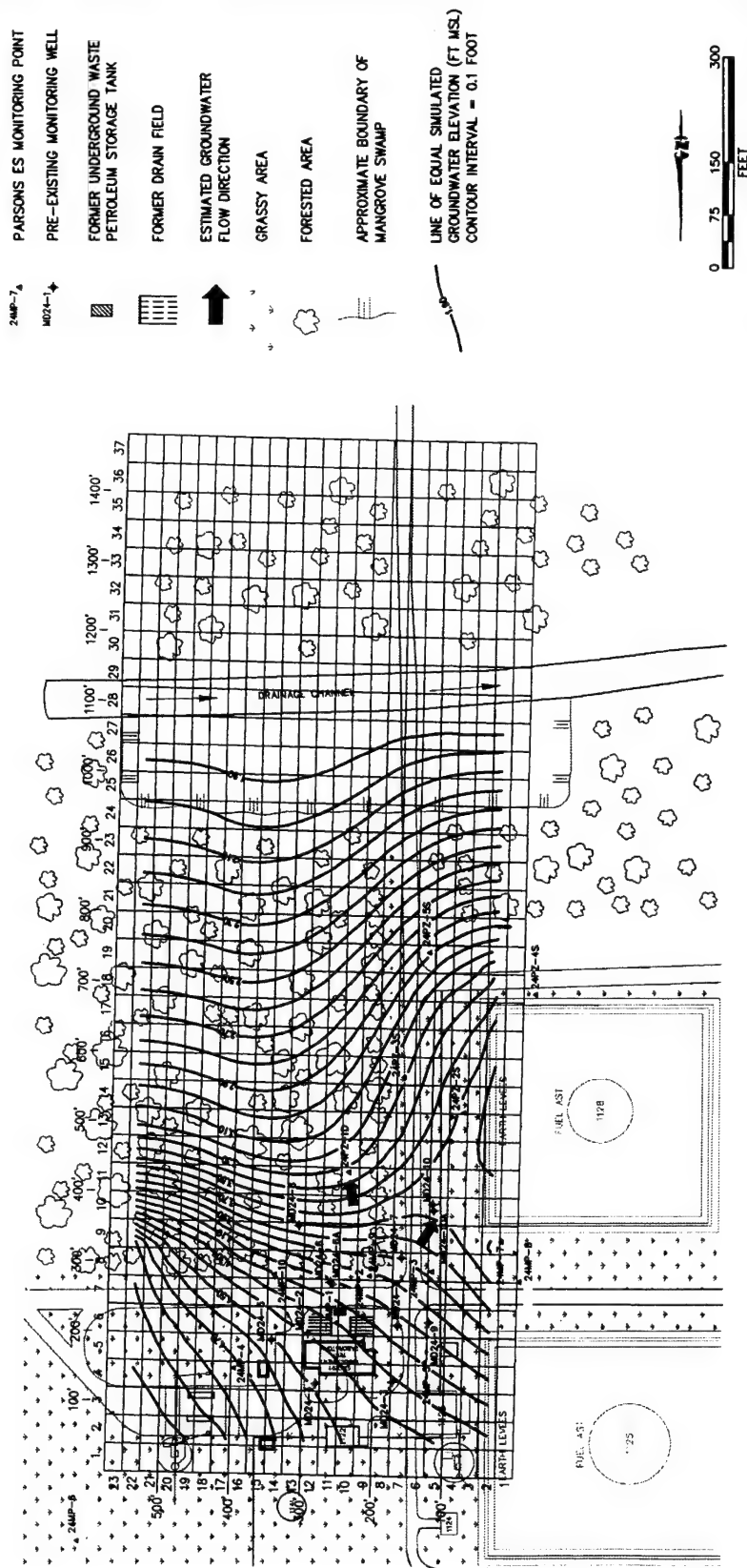


FIGURE 5.2
CALIBRATED
GROUNDWATER SURFACE

Site OT 24
 Intrinsic Remediation TS
 MacDill Air Force Base, Florida

PARSONS ENGINEERING SCIENCE, INC.
 Denver, Colorado

5.4.2 BTEX Plume Calibration

Model input parameters affecting the distribution and concentration of the simulated BTEX plume were modified so that model predictions were similar to dissolved total BTEX concentrations measured in March 1995. To do this, model runs were made using the calibrated steady-state hydraulic parameters. Calibration of the fate and transport portion of a Bioplume II model generally requires that the contaminant distribution be known for two different times. Due to the substantial differences between the dissolved BTEX plumes measured in 1988 through 1994 by CH2M Hill (1990 and 1991a) and Enserch Environmental (1994a and 1994b), and by Parsons ES in 1995 (see Section 5.3.3), a different calibration approach was used. The EMTL reportedly became operational in the early 1950s; however, the waste disposal and release history during the approximately 40 years of operation prior to removal of the drain fields in 1991 is unknown. For example, the date(s) of free product plume formation at the site is not known. For calibration purposes, it was assumed that, if all pertinent historical data were known, then an average BTEX source term concentration could be approximated for the period from the early 1950s to 1995. Therefore, BTEX source term concentrations and contaminant transport parameters in the model were varied in a trial and error fashion, and the model was run for a period of 42 years (from 1953 to 1995), until a reasonable simulation of the 1995 BTEX plume was achieved.

The partitioning of BTEX compounds from mobile and residual LNAPL into the groundwater was simulated by adding injection wells to the model. While the term "injection well" suggests that contaminants are being introduced at a point, Bioplume II assumes that contamination introduced at a well instantly equilibrates throughout the entire cell in which the well is located. The locations of simulated the injection wells are shown on Figure 5.3. Locations of simulated injection wells were based on the known locations of past contaminant sources such as the drain fields and former waste fuel UST, soil quality data obtained by CH2M Hill (1990), and the estimated distributions of mobile LNAPL and dissolved BTEX in groundwater. The injected BTEX concentrations were proportional to the groundwater BTEX concentrations measured in March 1995, with the maximum injected BTEX concentration occurring in the vicinity of the highest detected dissolved BTEX concentrations. The available data suggest that substantial contamination originated in the vicinity of the oil/water separator and eastern drain field; therefore, the highest BTEX injection concentration was located in this area. The injected BTEX concentrations were reduced in other areas where the measured BTEX concentrations in groundwater were lower. Due to the low DO concentrations measured in groundwater, the injected water was assumed to be oxygen-free. By varying the injection well concentrations, the anaerobic decay coefficient, the coefficient of retardation, and dispersivity, the BTEX plume was calibrated reasonably well to the existing plume in terms of plume extent and the magnitude and distribution of BTEX concentrations in the plume area. The injection rate for each well was set at 1×10^{-5} cubic foot per second (ft³/sec), a value low enough that the flow calibration and water balance were not affected.

The initial calibrated BTEX plume calculated by the model (Figure 5.4) is similar, but not identical, to the observed 1995 BTEX plume (Figure 4.4). For instance, the simulated plume extends further to the west than the observed 1995 plume. At monitoring point MD24-MP3S, the simulated BTEX concentration is slightly greater

LEGEND

- PARSONS ES MONITORING POINT
- PRE-EXISTING MONITORING WELL
- LOCATION OF SIMULATED BTEX INJECTION WELL
- FORMER UNDERGROUND WASTE PETROLEUM STORAGE TANK
- FORMER DRAIN FIELD
- GRASSY AREA
- FORESTED AREA
- APPROXIMATE BOUNDARY OF MANGROVE SWAMP

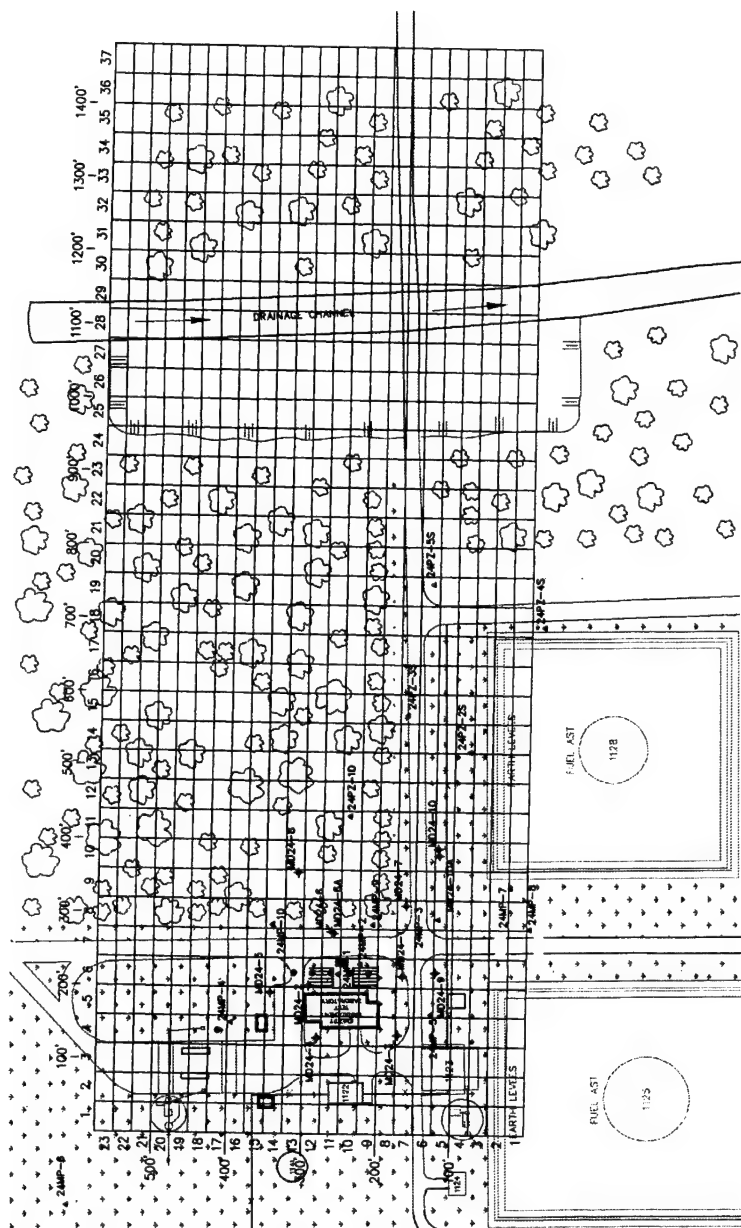


FIGURE 5.3

LOCATIONS OF SIMULATED INJECTION WELLS

Site OT 24
Intrinsic Remediation TS
MacDill Air Force Base, Florida

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Denver, Colorado

- LEGEND**
- 24MP-7a
 - 24MP-7b
 - PARSONS ES MONITORING POINT
 - PRE-EXISTING MONITORING WELL
 - FORMER UNDERGROUND WASTE PETROLEUM STORAGE TANK
 - FORMER DRAIN FIELD
 - ESTIMATED GROUNDWATER FLOW DIRECTION
 - GRASSY AREA
 - FORESTED AREA
 - APPROXIMATE BOUNDARY OF MANGROVE SWAMP
 - LINE OF EQUAL SIMULATED BTEX CONCENTRATION ($\mu\text{g/L}$)
 - CONTOUR INTERVAL = VARIABLE

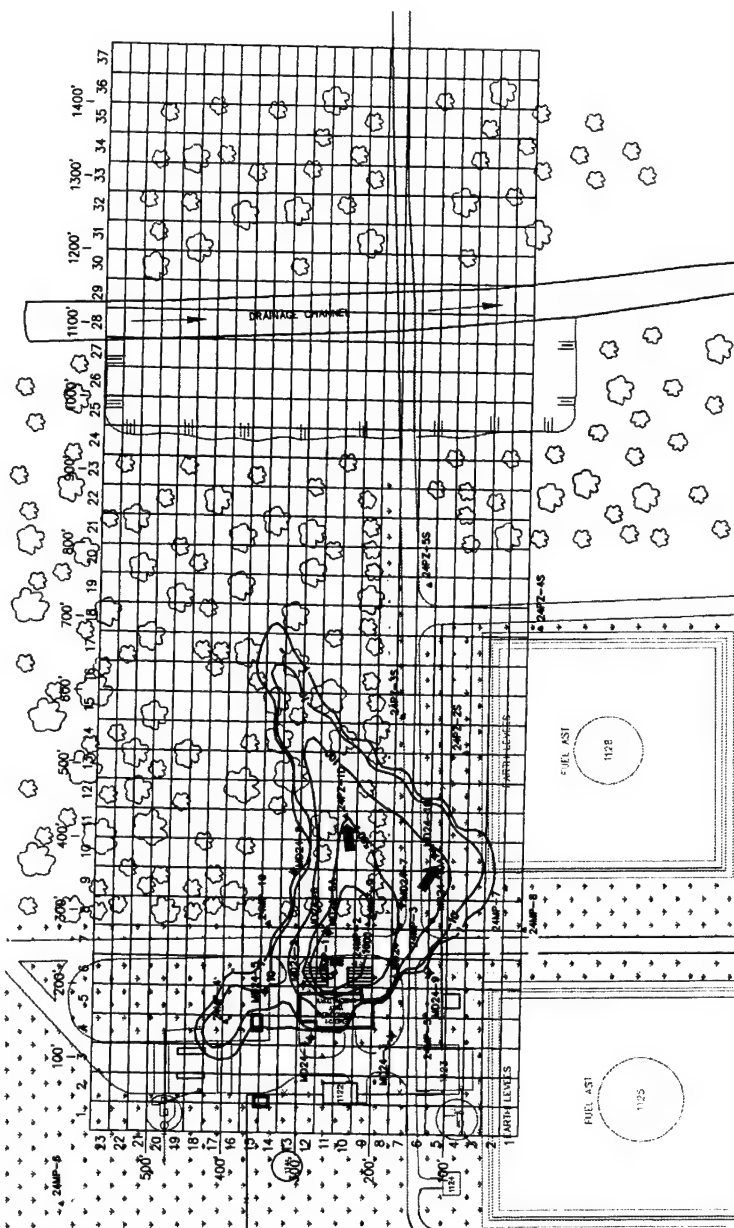


FIGURE 5.4

**INITIAL CALIBRATED
BTEX PLUME**

Site OT 24
Intrinsic Remediation TS
MacDill Air Force Base, Florida

**PARSONS
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Denver, Colorado

than 100 µg/L, whereas the measured concentration in March 1995 was 3.6 µg/L. Similarly, the simulated BTEX concentrations at many of the monitoring wells/points in the vicinity of and downgradient from the EMTL are higher than measured in 1995, contributing to the conservative nature of the model. The plume could be narrowed by increasing the anaerobic decay coefficient or the retardation coefficient, but this was not done in order to maintain the conservative nature of the model. The addition of oxygen to the recharge water in the western portion of the model domain also may contribute to a narrowing of the plume. However, as described in Section 5.3.4, oxygen was not added to the recharge water in the model.

Another difference between the simulated and measured BTEX plumes relates to the dissolved BTEX concentration of 22 µg/L detected at monitoring point 24MP-10S in March 1995. The source of the BTEX is not known, but may be related to the potential existence of a secondary, relatively minor BTEX source east-northeast of the EMTL (see Section 4.3.1.1). This detection was not reproduced by the model, but the low concentrations are considered to be insignificant relative to the BTEX concentrations present at and immediately south of the former drain fields. As described in Section 5.5.4, minor revisions were made to the initial calibrated model subsequent to and as a result of the sensitivity analyses.

As noted previously, the transport parameters varied during plume calibration were dispersivity, the anaerobic decay rate constant, and the coefficient of retardation. In addition, the BTEX source term injection concentrations were varied. These parameters generally were varied with intent of limiting plume migration to the observed extents, because the original estimates for the parameters resulted in a calculated BTEX plume that did not reasonably reproduce the original plume. These parameters are each discussed in the following paragraphs.

5.4.2.1 Dispersivity

Much controversy surrounds the concepts of dispersion and dispersivity. Longitudinal dispersivity was originally estimated as 50 feet, using one-tenth the distance between the plume source area and the estimated downgradient plume boundary, as defined by the 1-µg/L BTEX isopleth (Figure 4.4). As described in Section 4.3.1.1, the downgradient extent of the plume is not known due to the lack of monitoring stations in the forested area south of monitoring point 24PZ-1S. Therefore, this initial dispersivity estimate was speculative. Transverse dispersivity values generally are estimated as one-tenth (0.1) of the longitudinal dispersivity values (Domenico and Schwartz, 1990). However, because the 1995 plume was relatively narrow, the ratio of transverse to longitudinal dispersivity was reduced to 0.05. During plume calibration, the longitudinal dispersivity was reduced to 10 feet to better simulate the narrow linear shape of the BTEX plume. This is the value used to produce the initial calibrated plume depicted in Figure 5.4. As described in Section 5.5.4, during the subsequent sensitivity analyses, it was determined that increasing the dispersivity resulted in a significant decrease in the model's contaminant mass balance error without significantly affecting the quality of the plume calibration. Therefore, subsequent to the sensitivity analyses, the dispersivity was increased to 30 feet, which was the value used in the predictive model.

5.4.2.2 Anaerobic Decay Rate Constant

As discussed in Section 5.3.5, the anaerobic decay rate constant was estimated to range from 0.00037 day^{-1} to 0.00096 day^{-1} . This parameter was varied during plume calibration, and the calibrated model used a value of 0.0007 day^{-1} . Use of this intermediate value resulted in a simulated BTEX concentration in the vicinity of downgradient monitoring point 24PZ-1S that was similar to the measured concentration in that well, and that also allowed the maximum simulated BTEX concentration in the source area to resemble the maximum measured concentration in monitoring point 24MP-1S. The value of 0.0007 day^{-1} used in the calibrated model is believed to be reasonably conservative, as described in Section 5.3.5.

5.4.2.3 Coefficient of Retardation

Retardation of the BTEX compounds relative to the advective velocity of the groundwater occurs when BTEX molecules are sorbed to organic carbon, silt, or clay in the aquifer matrix. Based on measured TOC concentrations near the water table at four locations, an assumed bulk density of 1.6 grams per cubic centimeter (g/cc) (typical for sediments of this type), and published values of the soil sorption coefficient (K_{oc}) for the BTEX compounds (as listed in Wiedemeier *et al.*, 1995b), the coefficients of retardation for the BTEX compounds were calculated. The results of these calculations are summarized in Table 5.3. As described in Section 4.2.4, the highest measured TOC concentration (2.68 percent) was not used in these calculations in order to add to the conservative nature of the model. The lower the assumed coefficient of retardation, the farther the BTEX plume will migrate downgradient. To be conservative, the minimum range of retardation coefficients calculated for the BTEX compounds (1.00 to 5.40, for benzene) was used as a constraint for model input. Use of a retardation coefficient that is representative of benzene is realistic at this site because the BTEX detected at downgradient monitoring point 24PZ-1S consisted entirely of benzene.

The coefficient of retardation initially used as model input was 2.62, which was the average value computed for benzene (Table 5.3). During the plume calibration, this value was varied, and a value of 3.0 was used in the calibrated model. Similar to the anaerobic decay coefficient described above, use of this value allowed the simulated BTEX concentrations at downgradient monitoring point 24PZ-1S and in the source area at 24MP-1S to be similar to measured concentrations. Due to the probable occurrence of abundant root material in the shallow portion of the surficial aquifer beneath the forested area, the actual retardation of BTEX compounds in this portion of the model domain may be substantially greater.

5.4.2.4 Source Injection Concentration

Six injection wells were used to simulate the partitioning of BTEX from mobile and residual LNAPL in the vicinity of the plume. The water injection rate ($1 \times 10^{-5} \text{ ft}^3/\text{sec}$) was sufficiently low that the calibrated flow system was not altered. The injected BTEX concentrations were varied until the calibrated plume matched measured conditions reasonably well. During the calibration process, it became evident that maintenance of relatively high BTEX injection concentrations in this vicinity of

TABLE 5.3
CALCULATION OF RETARDATION COEFFICIENTS
SITE 0T 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Compound	K_{oc} (L/kg ^{a/})	Maximum Fraction Organic Carbon ^{b/}	Minimum Fraction Organic Carbon ^{b/}	Average Fraction Organic Carbon ^{b/}	Distribution Coefficient K_d (L/kg)		Bulk Density (kg/L) ^{d/}	Effective Porosity ^{e/}	Coefficient of Retardation	
					Maximum ^{e1/}	Minimum ^{e2/} Average ^{e3/}			Maximum	Minimum Average
Benzene	79	0.0087	0	0.0032	0.687	0.000 0.253	1.60	0.25	5.40	1.00 2.62
Toluene	190	0.0087	0	0.0032	1.653	0.000 0.608	1.60	0.25	11.58	1.00 4.89
Ethylbenzene	468	0.0087	0	0.0032	4.072	0.000 1.498	1.60	0.25	27.06	1.00 10.58
m-xylene	405	0.0087	0	0.0032	3.524	0.000 1.296	1.60	0.25	23.55	1.00 9.29
o-xylene	422	0.0087	0	0.0032	3.671	0.000 1.350	1.60	0.25	24.50	1.00 9.64
p-xylene	357	0.0087	0	0.0032	3.106	0.000 1.142	1.60	0.25	20.88	1.00 8.31

NOTES:

- ^{a/} From technical protocol (Wiedemeier *et al.*, 1995)
- ^{b/} From laboratory analyses of site soil samples
- ^{e1/} K_d = Maximum Fraction Organic Carbon x K_{oc}
- ^{e2/} K_d = Minimum Fraction Organic Carbon x K_{oc}
- ^{e3/} K_d = Average Fraction Organic Carbon x K_{oc}
- ^{d/} From laboratory analyses of moisture content, and assumed porosity and specific gravity.
- ^{e/} Literature value.

monitoring point 24MP-1S were necessary to simulate the measured dissolved BTEX concentration at that location.

5.5 SENSITIVITY ANALYSIS

The purpose of the sensitivity analysis is to determine the effect of varying model input parameters on model output. According to Rifai *et al.* (1988), the Bioplume II model is most sensitive to changes in the coefficient of reaeration, the anaerobic decay rate constant, and the hydraulic conductivity of the media, and is less sensitive to changes in the retardation factor, porosity, and dispersivity. The sensitivity analysis was conducted by varying transmissivity, the coefficient of retardation, the anaerobic decay rate constant, dispersivity, and BTEX injection concentrations. The coefficient of reaeration was not included in the sensitivity analyses because it was set to zero in the model. Use of a non-zero reaeration coefficient would make the model less conservative.

To perform the sensitivity analyses, the calibrated model was adjusted by systematically changing the aforementioned parameters individually, and then comparing the new simulations to the results of the original calibrated model. The models were run for a 42-year period, just as the original was, so that the independent effect of each variable could be assessed. Ten sensitivity runs of the calibrated model were made, with the following variations:

1. Transmissivity uniformly increased by a factor of 5;
2. Transmissivity uniformly decreased by a factor of 5;
3. Coefficient of retardation increased from 3.0 to 5.4;
4. Coefficient of retardation decreased from 3.0 to 1.0 (no retardation);
5. Anaerobic decay rate constant increased by a factor of 5;
6. Anaerobic decay rate constant decreased by a factor of 5;
7. Dispersivity increased by a factor of 5;
8. Dispersivity decreased by a factor of 5;
9. Injected BTEX concentrations increased by a factor of 5; and
10. Injected BTEX concentrations decreased by a factor of 5.

The results of the sensitivity analyses are shown in Figures 5.5 through 5.9. These figures display three-dimensional representations of modeled BTEX concentrations. The vertical axis of each three-dimensional figure represents the BTEX concentration in $\mu\text{g/L}$. As described in the following paragraphs, the parameter modifications listed above generally resulted in substantial changes in the resulting BTEX plumes, with the dispersivity modifications having the smallest effect.

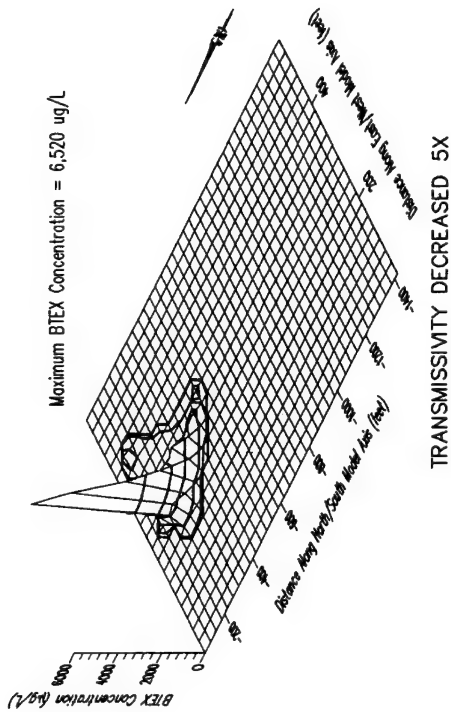
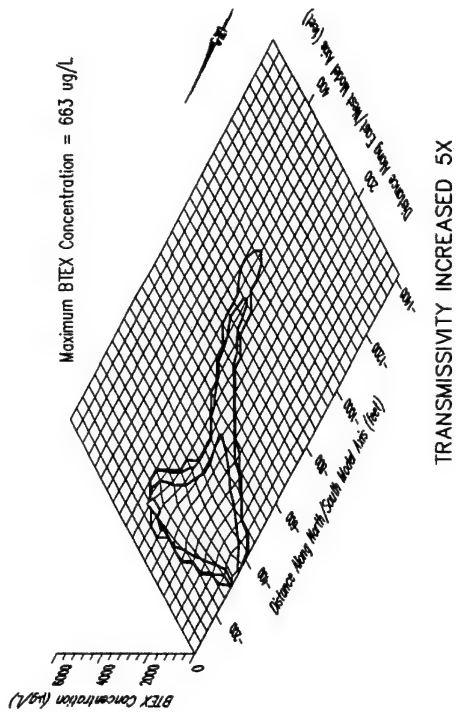
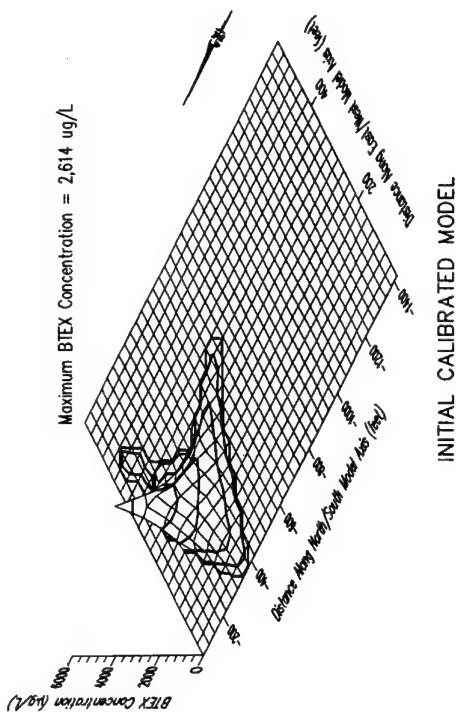


FIGURE 5.5
MODEL SENSITIVITY TO
VARIATIONS IN TRANSMISSIVITY

Site OT 24
Intrinsic Remediation TS
MacDill Air Force Base, Florida

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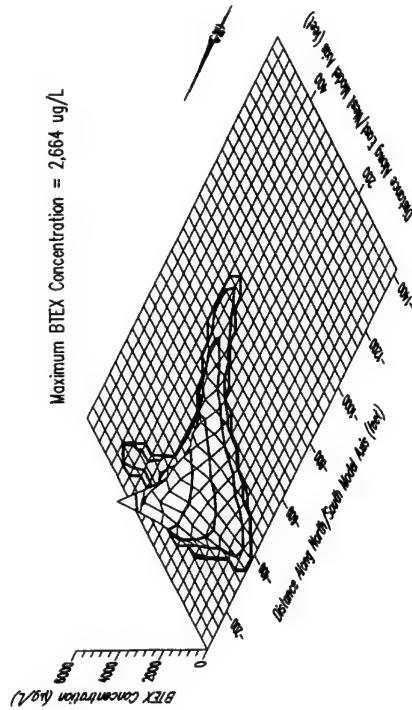
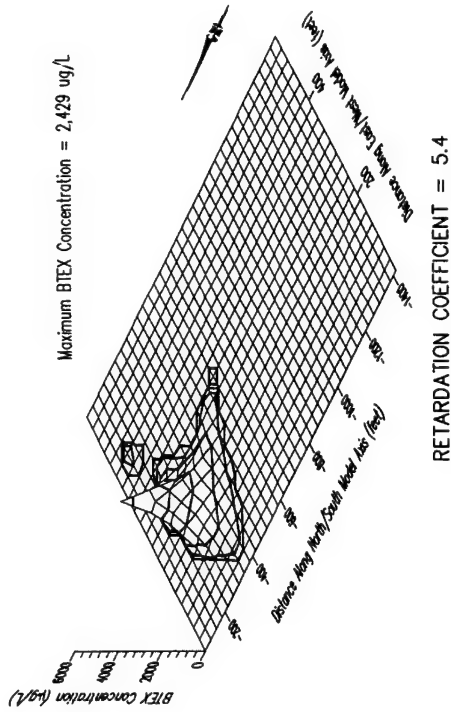
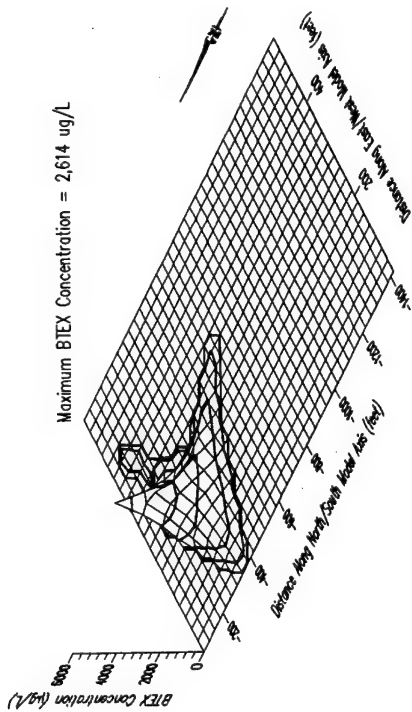


FIGURE 5.6
MODEL SENSITIVITY TO VARIATIONS IN RETARDATION COEFFICIENT
Site OT 24
Intrinsic Remediation TS
MacDill Air Force Base, Florida
PARSONS ENGINEERING SCIENCE, INC.
Denver, Colorado

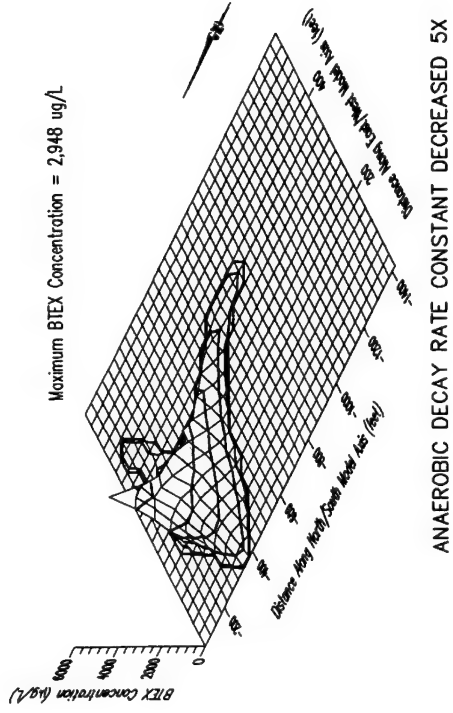
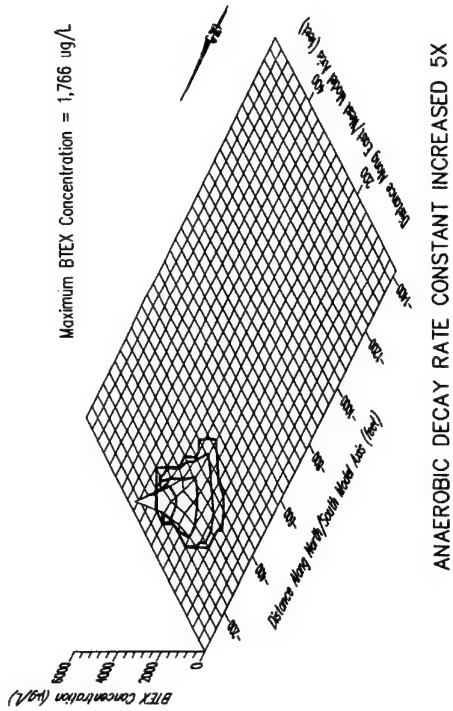
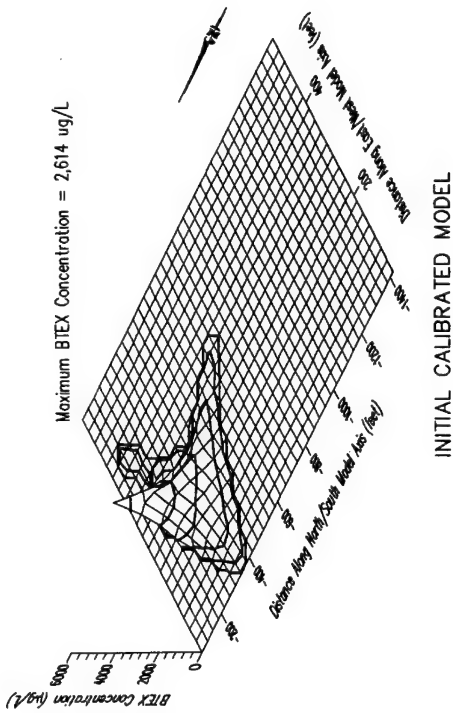


FIGURE 6.7
MODEL SENSITIVITY TO
VARIATIONS IN ANAEROBIC
DECAY RATE CONSTANT
 Site OT 24
 Intrinsic Remediation TS
 MacDill Air Force Base, Florida
PARSONS
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 Denver, Colorado

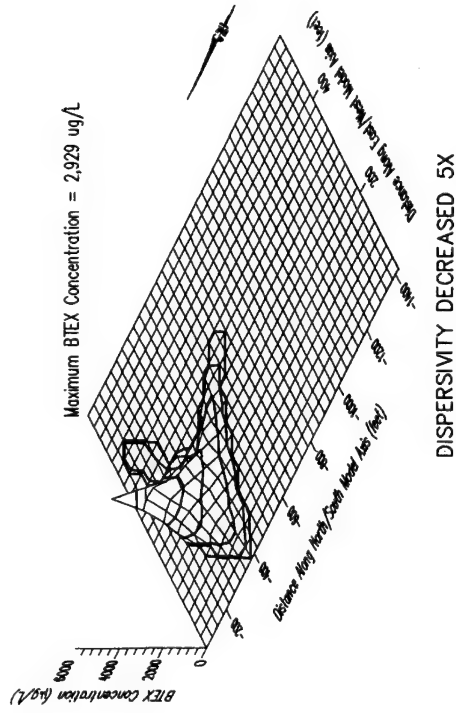
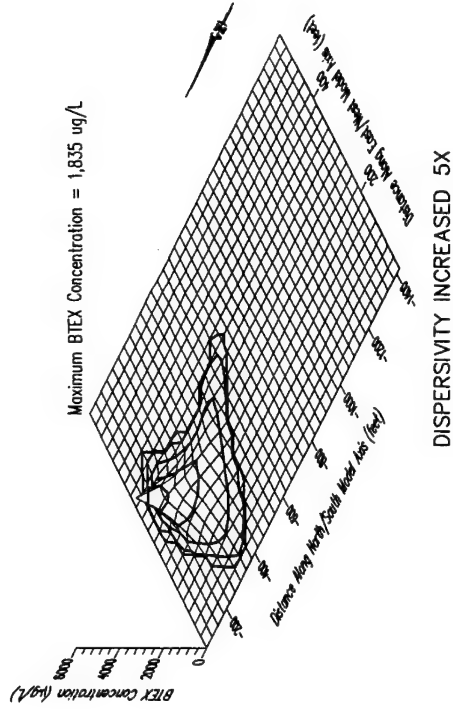
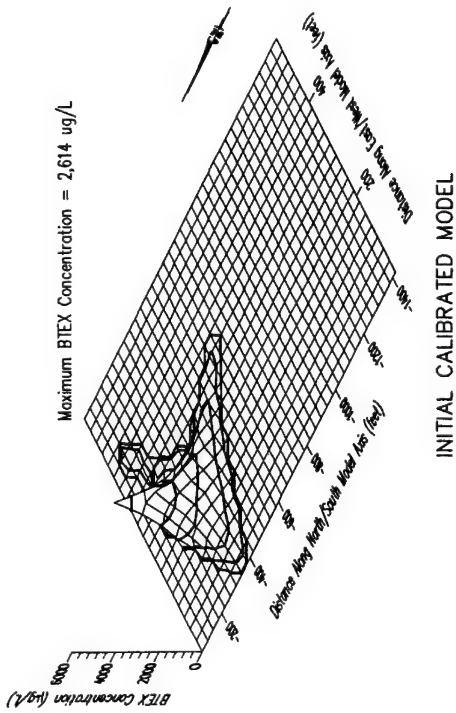


FIGURE 5.8
MODEL SENSITIVITY TO
VARIATIONS IN
DISPERSIVITY
 Site OT 24
 Intrinsic Remediation TS
 MacDill Air Force Base, Florida
PARSONS
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 Denver, Colorado

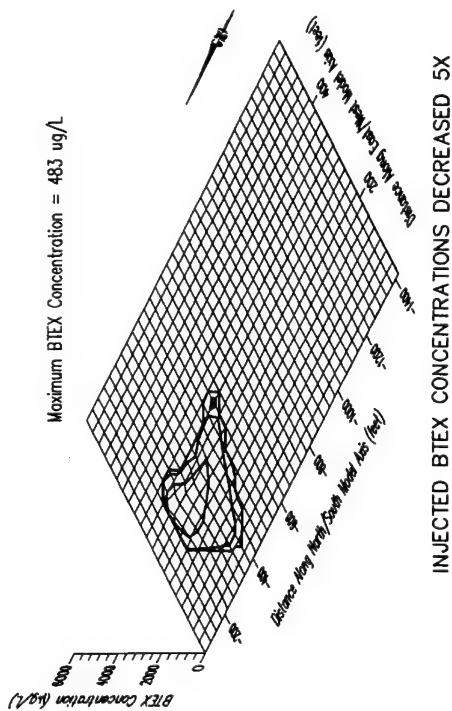
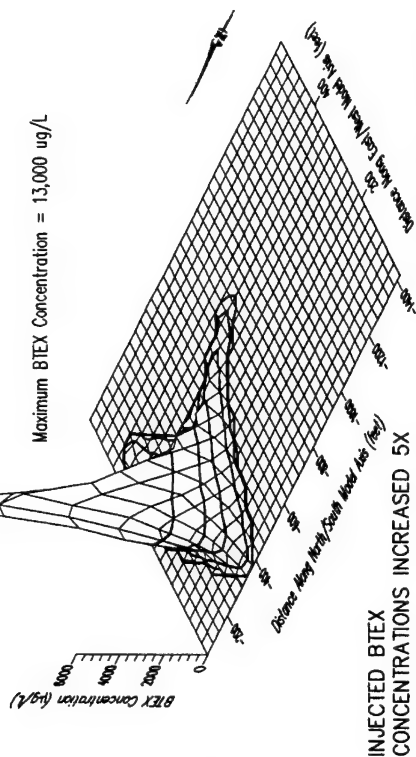
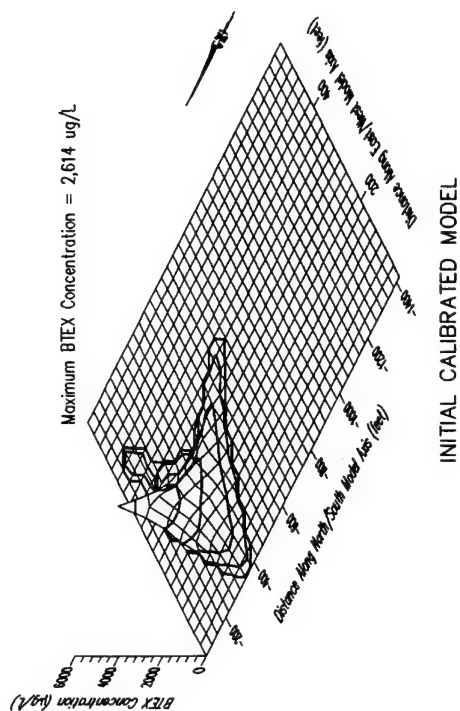


FIGURE 5.9

MODEL SENSITIVITY TO VARIATIONS IN INJECTED BTEX CONCENTRATIONS

Site OT 24
Intrinsic Remediation TS
MacDill Air Force Base, Florida

PARSONS ENGINEERING SCIENCE, INC.
Denver, Colorado

5.5.1 Sensitivity to Variations in Transmissivity

The effects of varying transmissivity are shown in Figure 5.5. Uniformly increasing the transmissivity by a factor of five increased the lateral dispersal of the plume such that the maximum observed BTEX concentration in the source cell area was only 663 $\mu\text{g/L}$, compared to the initial calibrated maximum of 2,614 $\mu\text{g/L}$. In addition, the leading edge of the BTEX plume advanced approximately 300 feet further downgradient than in the calibrated model. The faster groundwater velocity produced by the higher transmissivity initially results in greater plume travel rates and distances, diluting and further exposing the BTEX plume to electron acceptors.

In contrast, decreasing the transmissivity by a factor of five slowed overall plume migration, and caused the BTEX mass to be concentrated within a smaller area. As result, maximum BTEX levels in the source area increased to 6,520 $\mu\text{g/L}$. The simulated BTEX concentration at downgradient monitoring point 24PZ-1S was less than 10 $\mu\text{g/L}$, compared to a measured concentration of 180 $\mu\text{g/L}$.

5.5.2 Sensitivity to Variations in the Coefficient of Retardation

The effects of varying the coefficient of retardation (R) are shown on Figure 5.6. Increasing R causes the contaminant migration velocity to decrease relative to the advective groundwater velocity. This allows electron-acceptor-enriched groundwater to sweep through the BTEX plume to a greater degree, resulting in a corresponding decrease in dissolved BTEX concentrations. Increasing R to 5.4 from the value of 3.0 used in the calibrated model resulted in a plume configuration that was both shorter (by 90 feet) and narrower than the initial calibrated plume. This R value was the maximum value computed for benzene in Table 5.3. The maximum BTEX concentration in the source area was 2,429 $\mu\text{g/L}$, which is not substantially different from the calibrated maximum concentration of 2,614 $\mu\text{g/L}$. The simulated BTEX concentrations at downgradient monitoring stations MD24-6 and 24PZ-1S were approximately 900 $\mu\text{g/L}$ and 200 $\mu\text{g/L}$, respectively. These concentrations match the measured levels of 514 $\mu\text{g/L}$ (MD24-6) and 180 $\mu\text{g/L}$ (24PZ-1S) better than the concentrations simulated in the initial calibrated model (approximately 450 $\mu\text{g/L}$ for 24PZ-1S and 1,000 $\mu\text{g/L}$ for MD24-6). This observation, together with the narrowing of the plume obtained with the larger R value, indicated that use of a larger R value would result in a better calibration to observed conditions. As described in Section 5.4.2.1, root material in the saturated zone beneath the forested area may enhance the retardation of BTEX compounds. However, the R value of 3.0 was maintained in the calibrated model to enhance the downgradient migration of the plume and contribute to the conservative nature of the model.

Decreasing R to 1.0 (no retardation) produced a plume that was substantially longer (by approximately 160 feet) than the initial calibrated plume. The simulated BTEX concentration at downgradient monitoring point 24PZ-1S was greater than 1,000 $\mu\text{g/L}$, which appears to be unrealistically large based on available data. The maximum BTEX concentration in the source area was 2,664 $\mu\text{g/L}$, which is very similar to the concentration simulated by the initial calibrated model (2,614 $\mu\text{g/L}$).

5.5.3 Sensitivity to Variations in the Anaerobic Decay Rate Constant

Figure 5.7 shows the effects of varying the anaerobic decay rate constant. Increasing this parameter by a factor of five results in more rapid degradation of dissolved BTEX. The reduction in contaminant mass is the result of the relatively large increase in the decay rate caused by increasing the rate constant, because the anaerobic decay rate constant is exponentiated in the equation expressing the decay rate (see Section 5.3.5). The resulting BTEX plume has a relatively low maximum concentration of 1,766 $\mu\text{g/L}$, and is approximately 200 feet shorter than the initial calibrated plume. The plume barely reaches downgradient monitoring point 24PZ-1S (simulated concentration of approximately 10 $\mu\text{g/L}$), whereas this monitoring point had a measured BTEX concentration of 180 $\mu\text{g/L}$.

Conversely, decreasing the anaerobic decay rate constant by a factor of five decreases the rate of degradation, resulting in an overall increase in simulated downgradient BTEX concentrations to levels that were above observed concentrations. For example, the simulated BTEX concentration at monitoring point 24PZ-1S was approximately 1,400 $\mu\text{g/L}$, compared to a measured concentration of 180 $\mu\text{g/L}$. The resulting plume was approximately 200 feet longer than the plume simulated by the initial calibrated model.

5.5.4 Sensitivity to Variations in Dispersivity

The effects of varying dispersivity are illustrated in Figure 5.8. Both longitudinal and transverse dispersivity were varied for this analysis, as the ratio of the two values was kept constant at 0.050. Increasing the dispersivity by a factor of five resulted in a relatively low maximum BTEX concentration in the source area (1,835 $\mu\text{g/L}$), and an increase in concentrations upgradient from the source area above observed concentrations. In other respects however, the use of a larger dispersivity value resulted in a plume configuration that resembled the measured 1995 plume to an equal or better degree than the calibrated model. In addition, use of the larger value caused the contaminant mass balance error for the model to decrease from 22 percent to 8 percent. Decreasing the dispersivity by a factor of five produced a plume with an areal extent similar to the initial calibrated plume, but with slightly higher concentrations (maximum BTEX concentration of 2,929 $\mu\text{g/L}$). The relatively minor effect of this parameter adjustment can be attributed to the small magnitude of the dispersivity used in the initial calibrated model (10 feet), and the fact that decreasing this value by a factor of 5 did not substantially change the magnitude of this variable.

Based on these analyses, the model dispersivity was increased to 30 feet, and the strength of the BTEX source term in model grid cell (11,6) was also increased to maintain desired maximum dissolved BTEX concentrations in the source area. The resulting contaminant mass balance error was 13 percent. It was determined by trial and error that further combined increases in the dispersivity and BTEX source strength did not significantly improve the mass balance error, and caused upgradient contaminant concentrations to differ substantially from those measured in the field. The new calibrated plume configuration, shown in Figure 5.10, is nearly identical to the calibrated plume shown in Figures 5.4 through 5.9. However, use of the new plume for prediction purposes is more conservative given the higher BTEX injection concentrations in the source area.

- LEGEND**
- PARSONS ES MONITORING POINT
 - PRE-EXISTING MONITORING WELL
 - FORMER UNDERGROUND WASTE PETROLEUM STORAGE TANK
 - FORMER DRAIN FIELD
 - ESTIMATED GROUNDWATER FLOW DIRECTION
 - GRASSY AREA
 - FORESTED AREA
 - APPROXIMATE BOUNDARY OF MANGROVE SWAMP
 - LINE OF EQUAL SIMULATED BTEX CONCENTRATION ($\mu\text{g/L}$)
 - CONTOUR INTERVAL = VARIABLE

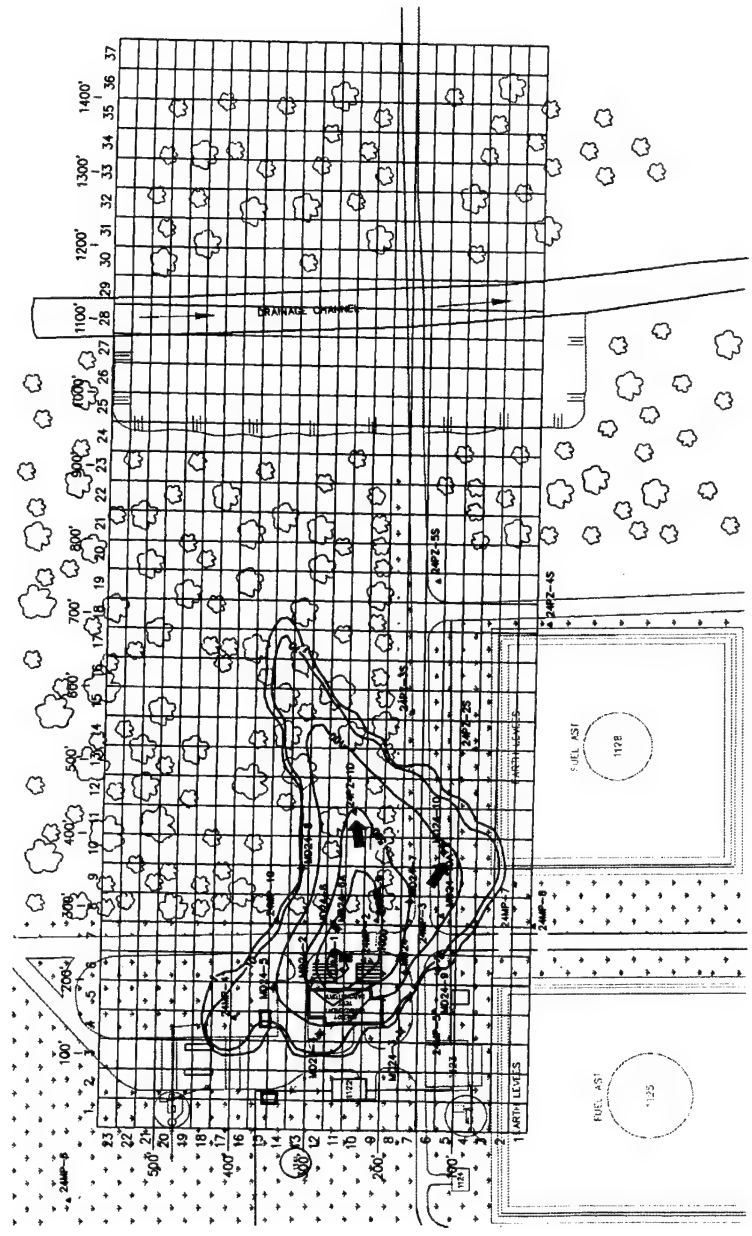


FIGURE 5.10
FINAL CALIBRATED BTEX PLUME
 Site OT 24
 Intrinsic Remediation TS
 MacDill Air Force Base, Florida
PARSONS ENGINEERING SCIENCE, INC.
 Denver, Colorado

5.5.5 Sensitivity to Variations in Injected BTEX Concentrations

The injected BTEX concentrations in the initial calibrated model ranged from 250 µg/L to 40,000 µg/L, with an injection rate of 1×10^{-5} ft³/sec. The results of increasing and decreasing the injected BTEX concentrations by a factor of five are shown on Figure 5.9. Increasing the injected concentrations by a factor of five nearly quintuples the maximum plume concentration to 13,000 µg/L, and generally substantially increases BTEX concentrations throughout the plume over those measured in the field. The resulting plume is approximately 110 feet longer than the initial calibrated plume. Decreasing the injected BTEX concentrations by a factor of five decreases the maximum simulated dissolved BTEX concentration by over 1,000 µg/L to 483 µg/L, and substantially decreases the area bounded by the 1-µg/L isopleth relative to the calibrated model. Based on these analyses, the model appears to be moderately to very sensitive to variations in injected BTEX concentrations of this magnitude, and the values used in the calibrated model appear to be reasonable.

5.5.6 Summary of Sensitivity Analysis Results

The results of the sensitivity analysis suggest that the calibrated model depicted in Figures 5.4 through 5.9 is reasonable. Varying the model parameters within the prescribed ranges generally caused the extent and magnitude of the dissolved BTEX plume to differ substantially from measured conditions. The greatest effects were observed when varying the transmissivity and BTEX injection concentrations within reasonable ranges, and the smallest effects were observed when varying the dispersivity. The sensitivity analyses did suggest that use of a larger retardation factor would improve the calibration of the model; however, the original (smaller) value was retained to add to the conservative nature of the model. The selected value is most representative of benzene in order to more effectively simulate the migration of this compound (which typically poses the most risk to potential receptors) to a greater degree than the other BTEX compounds. The analyses also revealed that use of a larger dispersivity, combined with an increase in the strength of the BTEX source term, would result in an improved contaminant mass balance error without adversely affecting the plume calibration. Therefore, these adjustments, which contribute to the conservatism of the model by increasing the BTEX source strength, were made in the calibrated model used for prediction (Figure 5.10). Only the transmissivity increase described above caused the BTEX plume to migrate to the potential surface discharge point at the mangrove swamp, supporting the prediction that the plume is not discharging to surface water downgradient of the EMTL.

5.6 MODEL RESULTS

To predict fate and transport of dissolved BTEX compounds at Site OT 24, three Bioplume II simulations (OT 24A, OT 24B, and OT 24C) were run using the calibrated, steady-state groundwater flow system. Complete input and output files are presented in Appendix D. Model results are described in the following sections. Model time for the predictive simulations is described using the term "simulation time," which refers to model time after the initial 42-year calibration period (i.e., simulation time after 1995).

The first simulation (OT 24A) assumed that the rates at which the BTEX compounds were introduced into the aquifer through injection wells geometrically decreased by 20 percent per year (injected BTEX concentrations were decreased by 20 percent from the concentration used for the previous year to account for natural weathering of fuel residuals). The derivation of this weathering rate is described in Section 5.6.1. At this rate, BTEX loading to the groundwater system was reduced by approximately 90 percent after 10 years.

The second simulation (OT 24B) assumes that all of the mobile and residual LNAPL in the model cells containing simulated injection wells are actively remediated via bioventing for 4 years, at the end of which the source area is no longer contributing BTEX to the groundwater. In this scenario, there is a 25-percent reduction in contaminant source term concentrations during each of the 4 years of system operation. This scenario assumes that, because the contaminated vadose zone soils have been largely excavated and removed from the site, the bioventing system would only be seasonally effective during low-water periods when contaminated soils below the average water table are unsaturated.

The third simulation (OT 24C) assumes that a groundwater extraction well pumping 2.5 gallons per minute (gpm) in model grid cell (11,6) (Figure 5.4) operates during the first 2 years of bioventing system operation. In their remedial action plan for the site, CH2M Hill (1991b) assumed a total pumping rate of 5 gpm for a 2-well extraction system. The extraction well removes both groundwater and dissolved BTEX from the surficial aquifer. Because groundwater pumping would depress the water table and expose residual LNAPL that is normally below the average water table, the effectiveness of the bioventing system would be enhanced. Therefore, the rate at which the contaminant source term concentrations are reduced was increased over the rate used in model OT 24B. Model OT 24C incorporates a 45-percent reduction in BTEX loading during each of the first 2 years of bioventing system operation, with the remaining 10 percent being remediated during the third year of system operation.

5.6.1 Diminishing BTEX Source (Model OT 24A)

To predict the fate and transport of dissolved BTEX compounds at Site OT 24, model OT 24A was run for a period of 30 years beyond 1995 (to calendar year 2025). Estimates of the current BTEX concentration in mobile LNAPL at the site were compared to the BTEX concentration of fresh JP-4 fuel to derive a feasible range of fuel weathering rates. As described in Section 4.1.2, the estimated BTEX concentration in fresh JP-4 fuel is 33,900 mg/L, and the BTEX concentration detected in the LNAPL sample obtained at the site is 25.4 mg/L, indicating that a substantial degree of weathering has occurred. Partitioning calculations (Appendix D) indicate that an LNAPL BTEX concentration of at least 6,045 mg/L is necessary to cause the maximum dissolved BTEX concentration measured in groundwater; therefore, the LNAPL sample analyzed at the laboratory may not accurately represent the BTEX concentration in mobile LNAPL at the site. These BTEX values suggest that nearly 28,000 mg/L of BTEX has been lost due to weathering, assuming that the fuel disposed of at the site was primarily JP-4. A lower-bound weathering rate of 696 mg/L per year (linear rate of 2 percent per year) can be calculated by assuming that the LNAPL was introduced to the subsurface 40 years ago (see calculations in Appendix D). Similarly, an upper-bound weathering rate of 3,979 mg/L per year (linear rate of 12 percent per

year) is obtained by assuming that the LNAPL was introduced shortly before EMTL discharge to the oil/water separator ceased in 1989.

Data collected from a petroleum product spill site at Eglin AFB, Florida that has climatic and hydrogeologic conditions similar to Site OT 24 indicates that the more rapid (upper-bound) weathering rate is most realistic. At that site, it was projected that the BTEX source LNAPL would disappear within 10 to 15 years due to the effects of weathering (Parsons ES, 1995d). To be conservative however, a linear weathering rate of 7 percent per year was used as a guide for the OT 24 Bioplume model. Using this rate, the mobile LNAPL BTEX source disappears 14 years after 1995 (calendar year 2009), or 20 years after the last potential release of product in 1989. A geometric weathering rate of 20 percent per year that achieves similar results (96-percent reduction rate by year 2009) was used in the model to simulate weathering of the BTEX source in mobile and residual LNAPL.

The temporal variations in the maximum dissolved BTEX concentrations in the plume are shown on Figure 5.11, and plume isopleth maps for simulation years 5, 10, and 15 are shown on Figure 5.12. The model indicates that the dissolved BTEX plume never migrates more than approximately 525 feet south of the EMTL (model grid column 18, Figure 5.1), and that the downgradient position of the plume remains constant as BTEX concentrations within the plume decrease over time. The maximum simulated dissolved BTEX concentration in the plume decreases steadily to below 50 µg/L during simulation year 21 (calendar year 2016), and the plume is completely biodegraded after 27 years of simulation time.

5.6.2 Engineered Source Reduction (Model OT 24B)

To illustrate the impact of engineered source reduction activities upon dissolved BTEX migration, model OT 24B incorporated more rapidly decreasing BTEX loading rates, assuming that bioventing or a similar *in situ* method would be used to remediate the source areas. Bioventing is an *in situ* process in which low-flow air injection is used to enhance the aerobic biodegradation of organic contaminants in subsurface soils by supplying oxygen to indigenous microbes. The model referenced above assumes complete remediation of vadose zone soils in the source area after 4 years. Bioventing tests at the Patrick AFB, Florida BX Service Station resulted in a BTEX removal rate of over 95 percent during the first year of testing (Parsons ES, 1995e). However, it is anticipated that a bioventing system at Site OT 24 would only be seasonally effective during low water periods when deeper contaminated soils are exposed above the water table.

Model OT 24B was run for a period of 25 years beyond 1995. As shown on Figure 5.13, this model predicts that the maximum dissolved BTEX concentrations in the plume would decrease to below 50 µg/L during simulation year 17 (calendar year 2012). The plume configurations through time predicted by model OT 24B are shown in Figure 5.14. After 22 years of simulation time, the BTEX plume is completely biodegraded.

If the bioventing well screen is placed very close to the average water table, then the well could serve as a biosparging well during high-water periods, and as a bioventing well during low-water periods. As a result, the DO content of the groundwater would

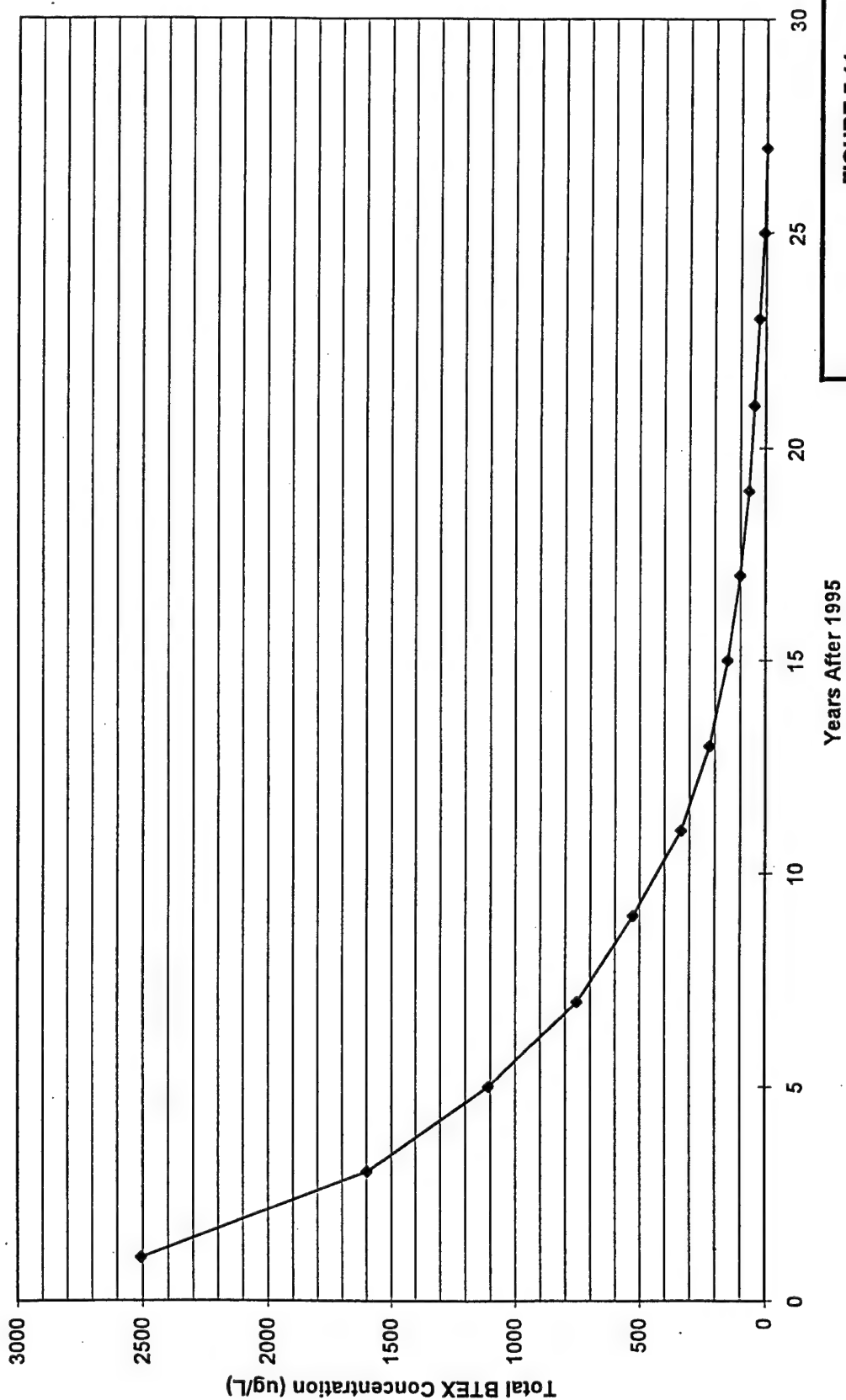


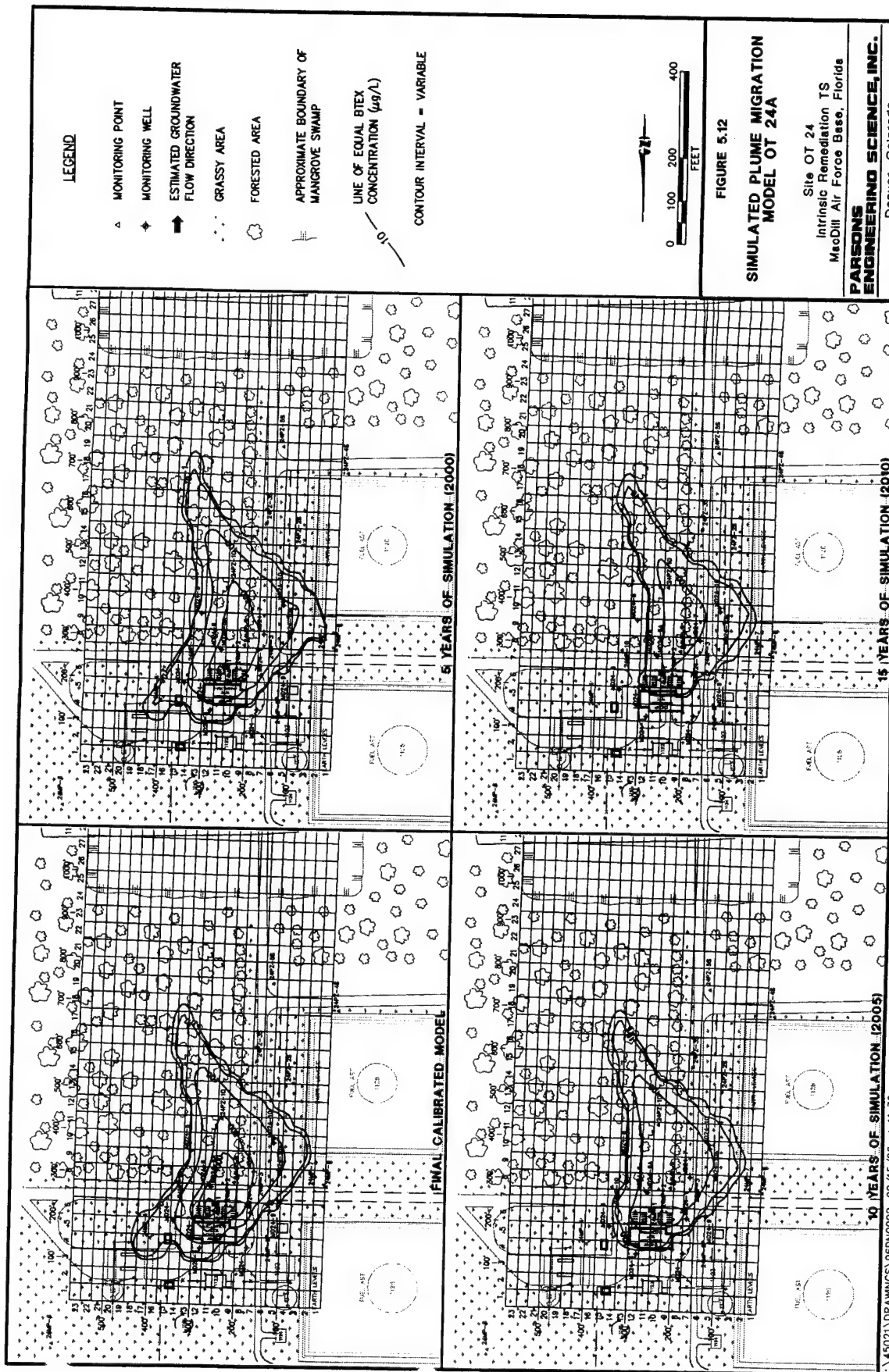
FIGURE 5.11

**SIMULATED MAXIMUM
BTEX CONCENTRATIONS
MODEL OT 24A**

Site OT 24
Intrinsic Remediation TS
MacDill Air Force Base, Florida



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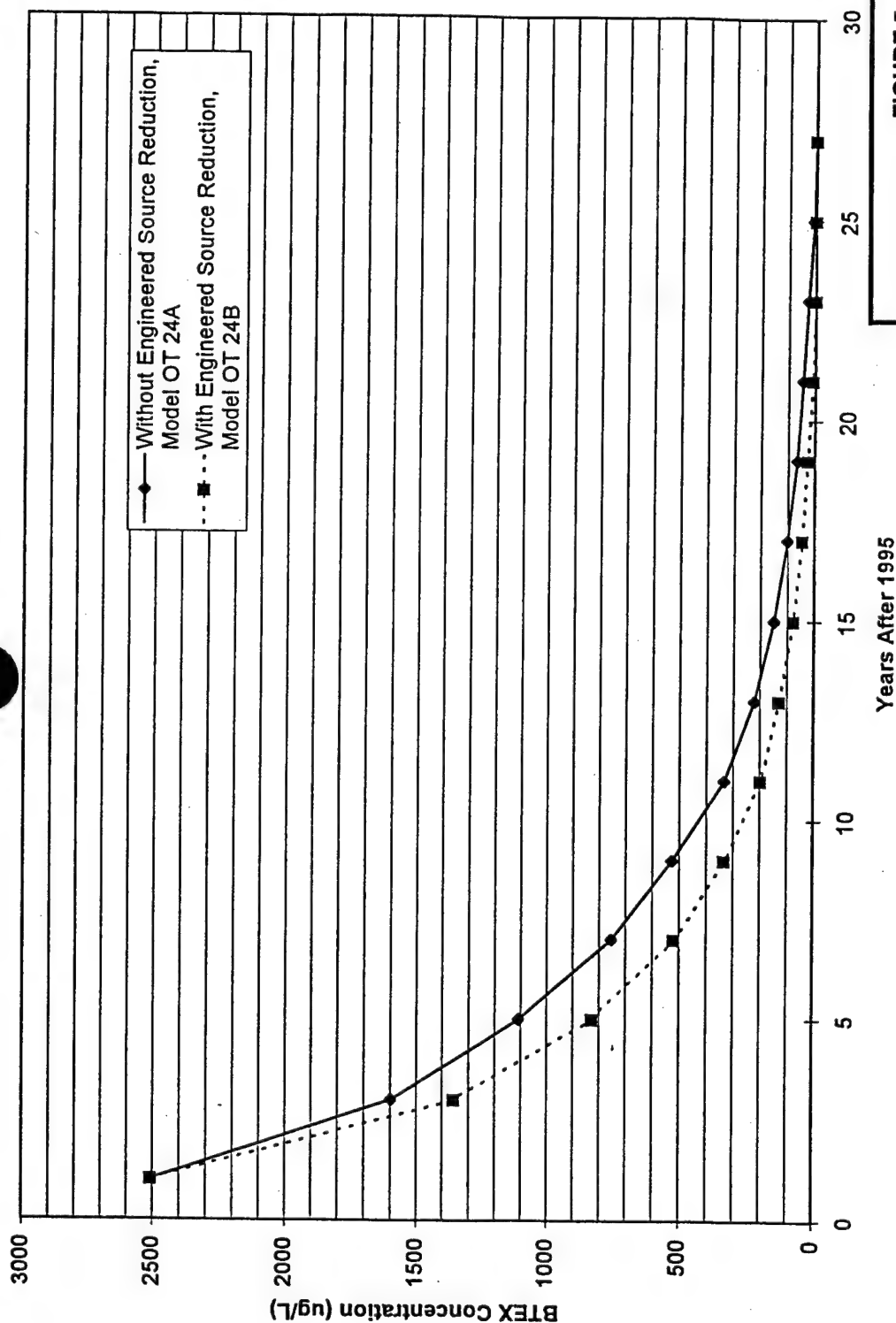


FIGURE 5.13

**SIMULATED MAXIMUM
BTX CONCENTRATIONS
MODELS OT 24A AND OT 24B**

Site OT 24

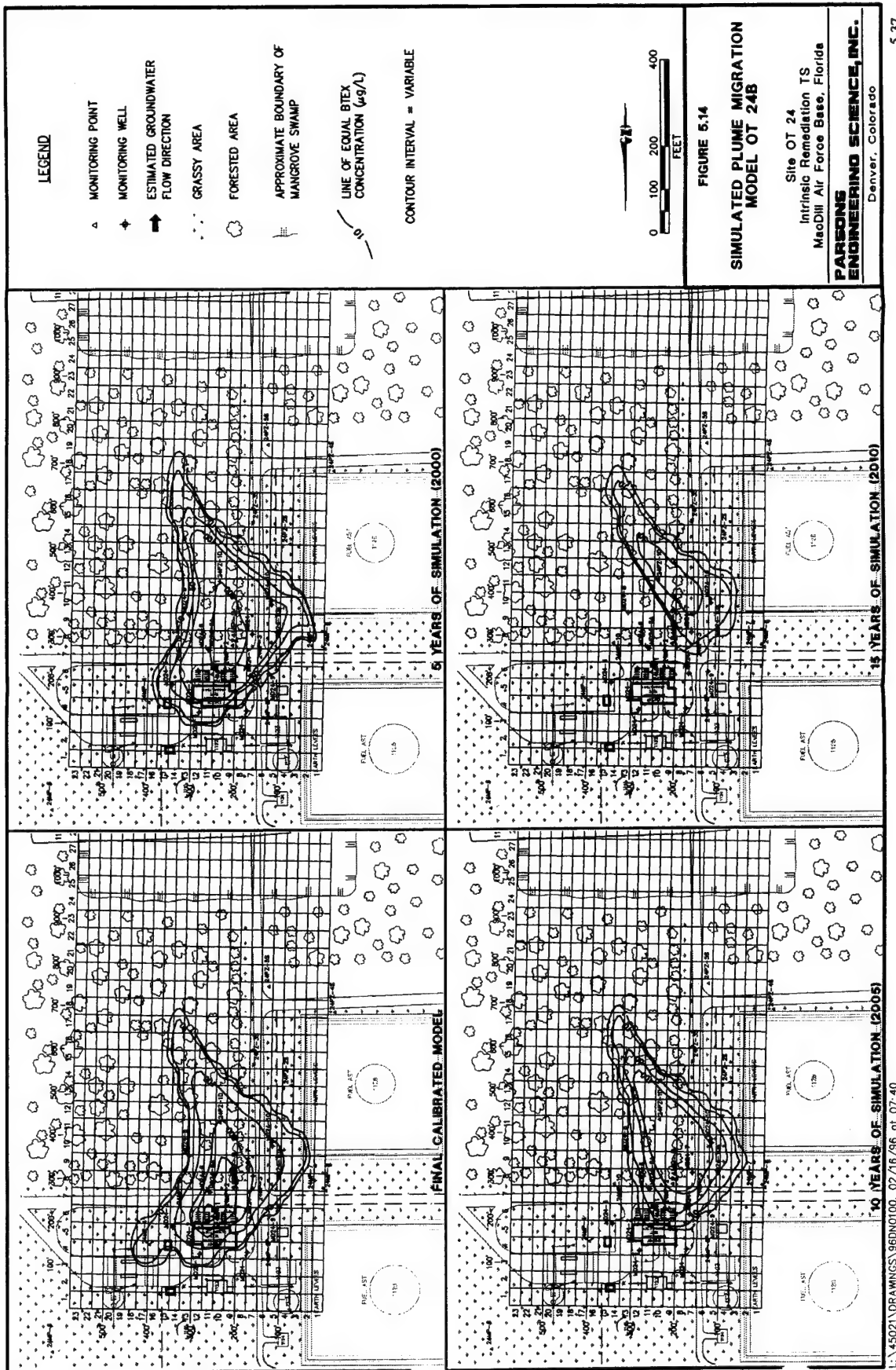
Intrinsic Remediation TS

MacDill Air Force Base, Florida



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be enhanced during high-water periods, promoting biodegradation of residual LNAPL below the average groundwater surface and enhancing the degradation of dissolved BTEX. In order to estimate the effect of this scenario on dissolved BTEX concentrations through time, oxygen was added to the injection water in source cell (11,6) during the 4-year period that the BTEX source is present and the remediation system is operating. To determine the proper amount of oxygen addition, varying amounts of DO were added to a model grid cell in an uncontaminated area [cell (20,5), Figure 5. 14] until the DO content of the groundwater in the cell increased by nearly 1 mg/L. The same amount of oxygen was then added to cell (11,6), and the model was run for a period of 25 years beyond 1995. Initially, the increased DO content of the groundwater had a noticeable effect on dissolved BTEX concentrations. For example, the BTEX concentration in cell (11,6) was nearly 300 µg/L lower after simulation year 1 than without oxygen addition to the groundwater. However, the model indicates that the maximum BTEX concentration migrates out of the oxygenated cell during simulation year 3. This migration, in combination with the cessation of oxygen injection after simulation year 4, diminishes the beneficial effect of oxygen addition, and by the end of simulation year 5 the maximum dissolved BTEX concentration is similar to that simulated without DO enhancement (model OT 24B). These results suggest that the DO enhancement over a 4-year period would not significantly reduce the time to site closure over that predicted by model OT 24B.

5.6.3 Engineered Source Reduction and Groundwater Extraction (Model OT 24C)

To illustrate the impact of both engineered source reduction and groundwater extraction in the plume "hotspot", model OT 24C incorporated one 2.5-gpm groundwater extraction well in model grid cell (11,6). This model assumes complete remediation of mobile/residual LNAPL in source area soils after 3 years. The well was operated during the first 2 years of bioventing system operation. The model was run for a period of 25 years beyond 1995. As shown on Figure 5.15, this model predicts that the maximum dissolved BTEX concentrations in the plume would decrease to below 1,000 µg/L during simulation year 2, and below 50 µg/L during simulation year 13. The plume configurations through time predicted by model OT 24C are similar to those shown for model OT 24B on Figure 5.14, with increased degradation rates. After 19 years of simulation time, the BTEX plume is completely biodegraded.

Simple batch-flushing calculations (Appendix D) were performed to estimate plume remediation times using an alternate method. These calculations simulate the partitioning of BTEX adsorbed to soil particles into the groundwater as clean groundwater from outside the plume area flushes through the zone of contaminated soils. The calculations indicate that the pumping should reduce source area dissolved BTEX levels to below 1,000 µg/L and 50 µg/L in 2 years and 7 years, respectively. Because elevated BTEX concentrations downgradient from the source area and the influence of the pumping system would take longer to naturally attenuate, these calculations indicate that it would take longer than 7 years but less than 17 years (see the discussion for model OT 24B, Section 5.6.2) for all BTEX concentrations within the plume to decrease below 50 µg/L. These results compare favorably with the results of model OT 24C. Experimentation with model OT 24C indicates that longer pumping times (e.g., 3 years) or greater numbers of wells [e.g., a second extraction well in grid cell (9,6)] would not significantly accelerate remediation times.

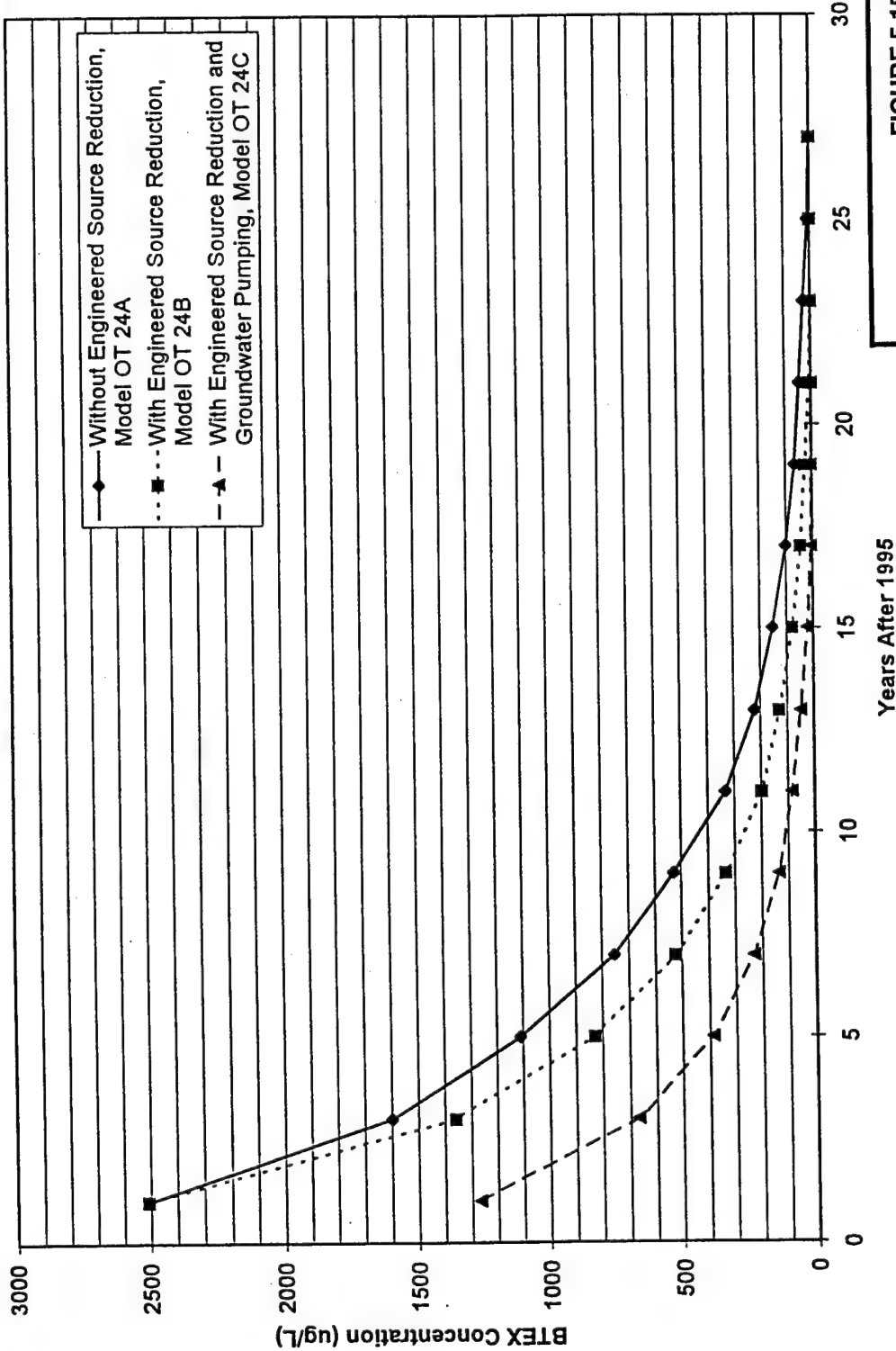


FIGURE 5.15

**SIMULATED MAXIMUM
BTX CONCENTRATIONS
MODELS OT 24A, OT 24B, AND OT 24C**

Site OT 24
Intrinsic Remediation TS
MacDill Air Force Base, Florida



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Denver, Colorado

5.7 CONCLUSIONS AND DISCUSSION

Three models were run to simulate a variety of conditions. Model OT 24A assumed natural attenuation of BTEX in mobile and residual LNAPL in source area soils. Model OT 24B was identical to OT 24A except that it simulated the effects of rapid remediation of source area soils through bioventing and a combination of bioventing and biosparging. Model OT 24C simulated the effects of source soil remediation and groundwater extraction in the plume "hotspot."

The results of the Bioplume II model simulations described in Section 5.6 suggest that the dissolved BTEX contamination will remain in the modeled area and decrease in concentration to below 50 µg/L after 21 years, even if no engineered remediation is performed. The modeling suggests that engineered remediation of source area soils would promote a more rapid decrease in dissolved BTEX concentrations, and the addition of groundwater extraction would result in a further decrease in the time to site closure [assumed to occur when total dissolved BTEX concentrations decrease to below 50 µg/L (see Section 6.2.3.3)].

The removal of dissolved BTEX compounds predicted by the simulations is largely a function of anaerobic biodegradation and sorption. Influxes of fresh groundwater enhance biodegradation by flushing water containing electron acceptors through the BTEX plume, which is retarded with respect to the advective groundwater velocity. As a result, biodegradation processes are maintained due to the continuous influx of electron acceptors. This is further enhanced by the additional influxes of electron acceptors in the grassy areas where precipitation recharge of the groundwater system occurs.

In all model simulations, several conservative assumptions are incorporated into the model. The use of these conservative model assumptions suggests that natural attenuation of BTEX contamination at the site may exceed model predictions. These conservative assumptions include the following:

1. Aerobic respiration, denitrification, iron reduction, sulfate reduction, and methanogenesis are all occurring at this site; however, only DO is considered as an electron acceptor during model simulations, and the anaerobic decay rate constant used in the calibrated model is lower than common literature values.
2. A low coefficient of retardation, which is most representative of benzene (3.0) was used for model simulations. The use of the low R value tends to increase the distance traveled by the simulated BTEX plume, but may provide a more accurate estimate of benzene transport relative to total BTEX. The sensitivity analyses described in Section 5.5.2 suggest that actual retardation in the surficial aquifer is higher than simulated by the Bioplume II model.
3. Oxygen was not added to the recharge water in the model.
4. A potentially conservative LNAPL weathering rate was used; therefore, dissolved BTEX may degrade to below applicable guidelines in shorter lengths of time than predicted by the model.

5. The BTEX mass in the simulated plume is greater than that indicated by field measurements, and simulated BTEX concentrations downgradient of the source area are higher than measured concentrations.

In summary, the strong geochemical evidence of anaerobic biodegradation, and the reasonably conservative nature of the Bioplume II models, suggest that natural attenuation will substantially reduce dissolved BTEX concentrations and limit plume migration. It is important to note that the modeled scenarios incorporate the assumption that additional inputs of contaminants to the subsurface through leaks or spills will not occur. The simulated injection wells are intended to represent continuing partitioning of BTEX from measured concentrations of mobile and residual LNAPL into the groundwater. Further definition of the downgradient extent of the BTEX plume in the forested area is recommended to ensure that contaminated groundwater is not discharging to surface water in the mangrove swamp, and to allow the plume to be monitored over time. Recommendations for additional investigations of this nature are described in Section 7.

SECTION 6

COMPARATIVE ANALYSIS OF REMEDIAL ALTERNATIVES

This section presents the development and comparative analysis of three groundwater remedial alternatives for Site OT 24 at MacDill AFB. The intent of this evaluation is to determine if intrinsic remediation is an appropriate and cost-effective remedial approach to consider when developing final remedial strategies for the site, especially when combined with other innovative and conventional remedial technologies.

Section 6.1 presents the criteria used to evaluate groundwater remedial alternatives. Section 6.2 discusses the development of remedial alternatives considered as part of this demonstration project. Section 6.3 provides a brief description of each of these remedial alternatives. Section 6.4 provides a more detailed analysis of the remedial alternatives using the defined remedial alternative evaluation criteria. The results of this evaluation process are summarized in Section 6.5.

6.1 REMEDIAL ALTERNATIVE EVALUATION CRITERIA

The evaluation criteria used to identify appropriate remedial alternatives for shallow groundwater contamination at the site were adapted from those recommended by the USEPA (1988) for selecting remedies for Superfund sites [Office of Solid Waste and Emergency Response (OSWER) Directive 9355.3-01]. These criteria included (1) long-term effectiveness and permanence, (2) technical and administrative implementability, and (3) relative cost. The following sections briefly describe the scope and purpose of each evaluation criterion. This report focuses on the potential use of intrinsic remediation and source reduction technologies to reduce BTEX and chlorinated solvent concentrations within the shallow groundwater to levels that meet regulatory standards intended to be protective of human health and the environment.

6.1.1 Long-Term Effectiveness and Permanence

Each remedial approach or remedial alternative (which can be a combination of remedial approaches such as intrinsic remediation and institutional controls) was analyzed to determine how effectively it will minimize groundwater plume expansion so that applicable groundwater quality standards can be achieved at a downgradient POC. The expected remedial effectiveness based on case histories from other sites with similar conditions also is evaluated. The ability to minimize potential impacts to surrounding facilities and operations is considered. Also, the ability of each remedial alternative to protect both current and potential future receptors from potential exposures associated with site-related contamination in shallow groundwater is

qualitatively assessed by conservatively evaluating the potential for completion of exposure pathways involving groundwater, either now or in the future. This evaluation criterion also included permanence and the ability to reduce contaminant mass, toxicity, and volume. Time to implementation and estimated time until protection is achieved are described. Long-term reliability for providing continued protection, including an assessment of potential for failure of the technology and the potential threats resulting from such a failure, also is evaluated.

6.1.2 Implementability

The technical implementation of each remedial technology/approach or remedial alternative was evaluated in terms of technical feasibility and availability. Potential logistical shortcomings and difficulties in construction, operations, and monitoring are presented and weighed against perceived benefits. Requirements for any post-implementation site controls such as LTM and land or groundwater use restrictions are described. Details on administrative feasibility in terms of the likelihood of public acceptance and the ability to obtain necessary approvals are discussed.

6.1.3 Cost

The total cost (present worth) of each remedial alternative was estimated for relative comparison following USEPA (1993) guidance. An estimate of capital costs, and operations and post-implementation costs for site monitoring and controls is included. An annual discount factor of 7 percent was assumed in present worth calculations (USEPA, 1993).

6.2 FACTORS INFLUENCING ALTERNATIVES DEVELOPMENT

Several factors were considered during the identification and screening of remedial technologies for addressing shallow groundwater contamination at the site. Factors considered included the objectives of the intrinsic remediation demonstration program; contaminant, groundwater, and soil properties; present and future land uses; and potential receptor exposure pathways. The following section briefly describes each of these factors and how they were used to narrow the list of potentially applicable remedial technologies to the final remedial alternatives considered for the site.

6.2.1 Program Objectives

The intent of the intrinsic remediation demonstration program sponsored by AFCEE is to develop a systematic process for scientifically investigating and documenting natural subsurface attenuation processes that can be factored into overall site remediation plans. The objective of this program and the specific Site OT 24 study is to provide solid evidence of intrinsic remediation of dissolved fuel hydrocarbons so that this information can be used to develop an effective groundwater remediation strategy. The intrinsic remediation of chlorinated solvents dissolved in the groundwater is also qualitatively discussed. A secondary goal of this multi-site initiative is to provide a series of regional case studies that demonstrate that natural processes of contaminant degradation can often reduce contaminant concentrations in groundwater to below

acceptable cleanup standards before completion of potential receptor exposure pathways.

Because the objective of this program is to study natural processes in the saturated zone rather than all contaminated media (soil, soil gas, etc.), approaches and technologies have been evaluated based primarily on their potential impact on shallow groundwater and phreatic soils. Technologies that can reduce vadose zone contamination and partitioning of contaminants into groundwater have also been evaluated. Many of the source removal technologies evaluated in this section will also reduce soil and soil gas contamination, but it is important to emphasize that the remedial alternatives developed in this document are not necessarily intended to remediate all contaminated media.

Additional program objectives set forth by AFCEE include cost effectiveness and minimization of waste. Approaches and technologies that may meet these criteria include institutional controls, soil vapor extraction, bioventing, biosparging, and intrinsic remediation. Soil excavation, slurry walls, sheet piling, carbon adsorption, *ex situ* biological or chemical treatment, and onsite/offsite disposal are generally not attractive technology candidates under this program.

6.2.2 Contaminant Properties

The site-related contaminants considered as part of this demonstration at Site OT 24 are the BTEX compounds. The CAH vinyl chloride was also considered in the remedial strategy. The source of the BTEX contamination is petroleum fuels present as mobile or residual LNAPL in capillary fringe and saturated soil in the vicinity of the EMTL. The exact type(s) of fuels are not known, but may include AVGAS and JP-4. The physiochemical characteristics of these fuels and the individual BTEX compounds will greatly influence the effectiveness and selection of a remedial technology.

Petroleum hydrocarbon mixtures, such as AVGAS and JP-4, are comprised of over 300 compounds with different physiochemical characteristics. These fuels are classified as a LNAPLs with liquid densities ranging from 0.73 to 0.80 g/cc at 20 °C (Arthur D. Little, Inc., 1987). Many compounds in these fuels sorb very well to soil and are concentrated in the capillary fringe because the mixtures are less dense than water. AVGAS and JP-4 are slightly soluble in water, with maximum solubilities ranging from 5 to 300 mg/L. These fuels are also a primary substrate for biological metabolism. Simultaneous biodegradation of aliphatic, aromatic, and alicyclic hydrocarbons has been observed. In fact, mineralization rates of hydrocarbons in mixtures such as JP-4 may be faster than mineralization of the individual constituents as a result of cometabolic pathways (Jamison *et al.*, 1975; Perry, 1984).

The BTEX compounds are generally volatile, highly soluble in water, and adsorb less strongly to soil than other hydrocarbons in a petroleum mixture. These characteristics allow the BTEX compounds to leach more rapidly from mobile LNAPL and contaminated soil into groundwater, and to migrate as dissolved contamination (Lyman *et al.*, 1992). All of the BTEX compounds are highly amenable to *in situ* degradation by both biotic and abiotic mechanisms.

Benzene is very volatile, with a vapor pressure of 76 millimeters of mercury (mm Hg) at 20°C and a Henry's Law Constant of approximately 0.0054 atm-m³/mol at 25°C (Hine and Mookerjee, 1975; Jury *et al.*, 1984). The solubility of pure benzene in water at 20°C has been reported to be 1,780 mg/L (Verschueren, 1983). Benzene is normally biodegraded to carbon dioxide, with catechol as a short-lived intermediate (Hopper, 1978; Ribbons and Eaton, 1992).

Toluene is also volatile, with a vapor pressure of 22 mm Hg at 20°C and a Henry's Law Constant of about 0.0067 atm-m³/mol at 25°C (Pankow and Rosen, 1988; Hine and Mookerjee, 1975). Toluene sorbs more readily to soil media relative to benzene, but still is very mobile. The solubility of pure toluene in water at 20°C is approximately 515 mg/L at 20°C (Verschueren, 1983). Toluene has been shown to degrade to pyruvate, acetaldehyde, and completely to carbon dioxide via the intermediate catechol (Hopper, 1978; Wilson *et al.*, 1986; Ribbons and Eaton, 1992).

Ethylbenzene has a vapor pressure of 7 mm Hg at 20°C and a Henry's Law Constant of 0.0066 atm-m³/mol (Pankow and Rosen, 1988; Valsaraj, 1988). Ethylbenzene tends to sorb more strongly to soils than benzene but less strongly than toluene (Abdul *et al.*, 1987). Pure ethylbenzene is also less soluble than benzene and toluene in water at 152 mg/L at 20°C (Verschueren, 1983; Miller *et al.*, 1985). Ethylbenzene ultimately degrades to carbon dioxide via its intermediate 3-ethylcatechol (Hopper, 1978; Ribbons and Eaton, 1992).

The three isomers of xylene have vapor pressures ranging from 7 to 9 mm Hg at 20°C and Henry's Law Constants of between 0.005 and 0.007 atm-m³/mol at 25°C (Mackay and Wolkoff, 1973; Hine and Mookerjee, 1975; Pankow and Rosen, 1988). Of all of the BTEX compounds, xylenes sorb most strongly to soil, but still can leach from soil into the groundwater (Abdul *et al.*, 1987). Pure xylenes have water solubilities of 152 to 160 mg/L at 20°C (Bohon and Claussen, 1951; Mackay and Shiu, 1981; Isnard and Lambert, 1988). Xylenes can degrade to carbon dioxide via pyruvate carbonyl intermediates (Hopper, 1978; Ribbons and Eaton, 1992).

The chlorinated solvents at Site OT 24 may be more resistant to biodegradation than the BTEX compounds. The primary mechanisms of attenuation for chlorinated solvents dissolved in the groundwater are adsorption, biodegradation, and volatilization to the vadose zone. Chlorinated compounds can be biodegraded via dechlorination and cometabolic processes (see Section 4). There are few microorganisms that are capable of growth using CAHs (e.g., TCE, DCE, DCA, and vinyl chloride) as a primary carbon source (Chapelle, 1993); furthermore, the majority of these microorganisms have only been observed in a controlled laboratory environment. The microorganisms that can facilitate degradation of CAHs in the soil and groundwater use the BTEX compounds as the primary carbon substrate.

Vinyl chloride is extremely volatile, with a vapor pressure of 2,580 mm of Hg at 20°C (Lyman *et al.*, 1982) and a Henry's Law Constant of 0.056 atm-m³/mol at 25°C (Hine and Mookerjee, 1975). Vinyl chloride does not adsorb as well as either TCE or DCE (Karickhoff *et al.*, 1979). It is more mobile than TCE, DCE, and benzene in groundwater. The solubility of vinyl chloride is about 1,100 mg/L at 25°C (Verschueren, 1983).

On the basis of these physiochemical characteristics, intrinsic remediation, soil vapor extraction, bioventing, biosparging/air sparging, groundwater extraction, and air stripping technologies could all be effective options for collecting, destroying, and/or treating BTEX and vinyl chloride at Site OT 24.

6.2.3 Site-Specific Conditions

Two general categories of site-specific characteristics were considered when identifying remedial technologies for comparative evaluation as part of this demonstration project. The first category was physical characteristics such as groundwater depth, gradient, flow direction, and soil type, which influence the types of remedial technologies most appropriate for the site. The second category involved assumptions about future land uses and potential exposure pathways. Each of these site-specific characteristics have influenced the selection of remedial alternatives included in the comparative evaluation.

6.2.3.1 Groundwater and Soil Characteristics

Site geology and hydrogeology will have a profound effect on the transport of contaminants and the effectiveness and scope of required remedial technologies at a given site. Hydraulic conductivity is perhaps the most important aquifer parameter governing groundwater flow and contaminant transport in the subsurface. The velocity of the groundwater and dissolved contamination is directly related to the hydraulic conductivity of the saturated zone. Aquifer tests conducted in the vicinity of Site OT 24 indicate a moderate conductivity within the sand unit present in the vicinity of the source area and dissolved plume. Estimated conductivity values ranged from less than 1 to 57 ft/day, characteristic of sand or silty sand.

Although higher hydraulic conductivities can result in plume expansion and migration, this same characteristic also will decrease the average BTEX concentration within the plume and enhance the effectiveness of other remedial technologies, such as groundwater extraction, biosparging, and intrinsic remediation. For example, it should be less expensive and time-consuming to capture and treat the contaminant plume using extraction wells in areas of high hydraulic conductivity. Contaminant recovery also may be maximized when contaminants are not significantly sorbed to and retarded by phreatic soil. The effectiveness of biosparging may also be increased in highly conductive aquifers because of reduced entry pressures and increased radius of influence for each biosparging point. Greater hydraulic conductivity also would increase the amount of contaminant mass traveling through a biosparging network. The DO introduced through biosparging can enhance aerobic degradation of the dissolved contaminant mass, particularly at sites such as OT 24 where oxygen-deficient groundwater predominates.

The movement of contaminants within the subsurface away from the source also will increase the effectiveness of natural biodegradation processes by distributing the contaminant mass into areas enriched with electron acceptors. In addition, because BTEX compounds are retarded relative to the advective flow velocity, relatively fresh groundwater containing DO and other electron acceptors will migrate through the plume area, further increasing biodegradation.

To satisfy the requirements of indigenous microbial activity and intrinsic remediation, the aquifer must also provide an adequate and available carbon or energy source, electron acceptors, essential nutrients, and proper ranges of pH, temperature, and redox potential. Data collected as part of the field work phase of this demonstration project and described in Sections 3 and 4 of this document indicate that this site is characterized by adequate and available carbon/energy sources and electron acceptors to support measurable biodegradation of fuel hydrocarbon contamination by indigenous microorganisms. Sulfate and carbon dioxide (which is utilized during methanogenesis) represent primary sources of electron acceptor capacity for the biodegradation of BTEX compounds at the site. Relatively minor electron acceptors include DO and ferric iron. Further, because fuel-hydrocarbon-degrading microorganisms have been known to thrive under a wide range of temperature and pH conditions (Freeze and Cherry, 1979), the physical and chemical conditions of the groundwater and phreatic soil at the site are not likely to inhibit microorganism growth.

Fuel-hydrocarbon-degrading microorganisms are ubiquitous, and as many as 28 hydrocarbon-degrading isolates (bacteria and fungi) have been identified in different soil environments (Davies and Westlake, 1977; Jones and Eddington, 1968). Indigenous microorganisms have a distinct advantage over microorganisms injected into the subsurface to enhance biodegradation because indigenous microorganisms are well adapted to the physical and chemical conditions of the subsurface in which they reside (Goldstein *et al.*, 1985). Therefore, microbe addition was not considered a viable remedial approach for this site.

6.2.3.2 Potential Exposure Pathways

A pathways analysis identifies the human and ecological receptors that could potentially come into contact with site-related contamination and the pathways through which these receptors might be exposed. To have a completed exposure pathway, there must be a source of contamination, a potential mechanism(s) of release, a pathway of transport to an exposure point, an exposure point, and a receptor. If any of these elements do not exist, the exposure pathway is considered incomplete, and receptors will not come into contact with site-related contamination. Evaluation of the potential long-term effectiveness of any remedial technology or remedial alternative as part of this demonstration project includes determining if the approach will be sufficient and adequate to minimize plume expansion so that potential receptor exposure pathways involving shallow groundwater contaminants are not completed.

Assumptions about current and future land uses at a site form the basis for identifying potential receptors, potential exposure pathways, reasonable exposure scenarios, and appropriate remediation goals. USEPA (1991) advises that the land use associated with the highest (most conservative) potential level of exposure and risk that can reasonably be expected to occur should be used to guide the identification of potential exposure pathways and to determine the level to which the site must be remediated.

Site OT 24 is located immediately south of the northern Base property boundary. The current land use at the site is industrial. The primary contamination source area appears to be the approximately 5,000-square-foot grassy area immediately south of the

EMTL, which previously contained drain fields, a waste petroleum UST, and an oil/water separator. The nearest off-Base development appears to be a residential area located approximately 700 feet northwest of (hydraulically upgradient to crossgradient from) the EMTL (Figure 1.2). The site is bordered on the west and southwest by a fuel tank farm, which has dimensions of approximately 1,200 feet in the east/west direction and 800 feet in the north/south direction. Sparse development consisting of nonresidential Base buildings and storage yards are present approximately 600 feet east of Site OT 24. Therefore, the current land use within and downgradient of the contaminant plume is entirely commercial/industrial.

The area south of the tank farm is undeveloped for approximately 1,000 feet. The area immediately south of the contamination source area is occupied by a forest for a distance of approximately 750 feet. A mangrove swamp borders the forest on the south, and an east/west-trending drainage channel borders the mangrove swamp on the south, approximately 900 feet south of the EMTL. The channel depth ranges from approximately 5 to 6 feet bgs. Groundwater in the shallow portion of the surficial aquifer probably discharges to the mangrove swamp; however, it is also possible that some groundwater underflow beneath the swamp occurs. The 5- to 6-foot deep drainage channel bordering the swamp on the south represents an additional probable discharge area for shallow groundwater in the surficial aquifer. The swamp and drainage channel may represent natural hydraulic boundaries to further migration of the BTEX plume. Water in the ditch flows westward approximately 4,000 feet via a series of ditches into Tampa Bay.

Under reasonable current land use assumptions, potential receptors include only Base worker populations and forest vegetation, because the Bioplume II model results indicate that the dissolved BTEX plume will not migrate far enough to pose a threat to potential receptors exposed to surface water at the swamp or the drainage channel, and will not migrate off Base. Workers could be exposed to site-related contamination in phreatic soils or shallow groundwater if these materials are removed or exposed during future construction excavations or remedial activities. Groundwater from the shallow aquifer is not currently used to meet any demands at MacDill AFB. All Base potable water is supplied by the City of Tampa. There are no private wells located on the Base, and the Hillsborough County designated Wellhead Protection Area nearest to Site OT 24 is located approximately 13 miles north of the Base (BVWS, 1995). The nearest private well reportedly is located approximately 0.3 mile north (hydraulically upgradient) of the site (ES, 1988). Exposure pathways involving other environmental media such as vadose zone soils and soil gas in the source area were not considered as part of this project, but should be considered in overall site remediation decisions.

Forest vegetation may be exposed to contaminants in groundwater via uptake through root systems that penetrate the water table. However, available data indicate that dissolved BTEX concentrations in the groundwater beneath the forested area are not high enough to adversely affect the forest vegetation. For example, the vegetative "lowest effect level" for xylenes in solution is reported to be 100 mg/L (Allen *et al.*, 1961). The lowest effect level for toluene in soil is 200 mg/kg (Overcash *et al.*, 1982).

Assumptions about hypothetical future land uses also must be made to ensure that the remedial technology or alternative considered for shallow groundwater at the site is

adequate and sufficient to provide long-term protection. The future use of Site OT 24 and the surrounding area is projected to be unchanged from the current uses described above. Therefore, potential future receptors are the same as those listed in the preceding paragraph. The potential future exposure pathways involving Base workers are identical to those under current conditions provided shallow groundwater is not used to meet industrial water demands. In summary, the use of the intrinsic remediation approach at this site will require that the source area be maintained as industrial property and that restrictions on shallow groundwater use be enforced in areas downgradient from the site until natural attenuation reduces contaminants to concentrations that meet regulatory standards. If source removal technologies such as soil vapor extraction, bioventing, biosparging, or groundwater pump and treat are implemented, they will have some impact on the short- and long-term land use options and will require some level of institutional control and worker protection during remediation.

6.2.3.3 Remediation Goals for Shallow Groundwater

The results of model OT 24A suggest that BTEX compounds are not likely to move more than approximately 550 feet downgradient from the EMTL. Therefore, an area approximately 650 feet downgradient from the EMTL has been identified as the POC for groundwater remedial activities because this is beyond the projected maximum extent of future contaminant migration and upgradient from potential groundwater discharge points (i.e., the swamp and the drainage channel). This is a suitable location for monitoring and for demonstrating compliance with protective groundwater quality standards.

This remedial strategy assumes that compliance with promulgated, single-point remediation goals is not necessary if site-related contamination does not pose a threat to human health or the environment (i.e., exposure pathways are incomplete). Thus, the magnitude of required remediation in areas that can and will be placed under institutional control is different from the remediation that is required in areas that may be available for unrestricted use. The primary remedial action objective (RAO) for shallow groundwater at and downgradient of Site OT 24 is limiting plume expansion to prevent exposure of downgradient receptors to concentrations of BTEX and CAHs in groundwater and/or surface water at levels that exceed regulatory standards or guidelines. This means that viable remedial alternatives must be able to achieve concentrations that minimize plume migration and/or expansion. The ultimate RAO for BTEX in shallow groundwater at the POC is attainment of state no-further-action guidelines for G-II groundwater in an area where there are no drinking water wells within 0.25 mile of the site, and no public water supply wells within 0.50 mile of the site. These guidelines are contained in *No Further Action and Monitoring Only Guidelines for Petroleum Contaminated Sites* (FDER, 1990), and are summarized in Table 6.1. An interim BTEX RAO for attainment of "monitoring only" status for shallow groundwater are the "monitoring only" guidelines presented by FDER (1990). These interim guidelines could be used to determine when to discontinue an aggressive remedial action such as source removal via bioventing or a groundwater pump-and-treat system and allow intrinsic remediation with monitoring to remediate to no-further-action levels. Applicable regulatory standards for CAHs in groundwater (i.e., vinyl

TABLE 6.1
POINT-OF-COMPLIANCE REMEDIATION GOALS FOR
GROUNDWATER
SITE 0T 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Compound	No Further Action Groundwater RAO ^{a/} (µg/L) ^{b/}	Monitoring Only Groundwater RAO (µg/L)
Benzene	50	50 (perimeter) 500 (source area)
Total BTEX ^{c/}	50	50 (perimeter) 1,000 (source area)
Vinyl Chloride	1	NA ^{d/}

Sources: FDER, 1990 (benzene, BTEX).
FDER, 1989 (vinyl chloride).

^{a/} RAO = remedial action objective.

^{b/} µg/L = micrograms per liter.

^{c/} BTEX = benzene, toluene, ethylbenzene, and xylenes.

^{d/} NA = not applicable.

chloride) must also be met at this site. Available data suggest that vinyl chloride is the CAH of primary concern (Table 6.1).

In summary, available data suggest that there is no completed potential exposure pathway involving shallow groundwater under current conditions. Moreover, it is likely that no additional potential exposure pathways involving shallow groundwater would be completed under future land use assumptions, provided use of shallow groundwater as a potable or industrial source of water is prohibited by institutional controls within and downgradient from the BTEX plume to the drainage channel. Thus, institutional controls are likely to be a necessary component of any groundwater remediation strategy for this site. The required duration of these institutional controls may vary depending on the effectiveness of the selected remedial technology at reducing contaminant mass and concentration in the groundwater.

6.2.4 Summary of Remedial Option Screening

Several remedial options were identified and screened for use in treating the shallow groundwater at the site. Table 6.2 identifies the initial remedial technologies considered as part of this demonstration and those retained for detailed comparative analysis. Screening was conducted systematically by considering the program objectives of the AFCEE intrinsic remediation demonstration, physiochemical properties of the BTEX and chlorinated solvent compounds, and other site-specific characteristics such as hydrogeology, land use assumptions, potential receptors and exposure pathways, and appropriate remediation goals. All of these factors will influence the technical effectiveness, implementation, and relative cost of technologies for remediating shallow groundwater underlying and migrating from the site. The remedial approaches and source removal technologies retained for development of remedial alternatives and comparative analysis include institutional controls, intrinsic remediation combined with LTM, bioventing/biosparging, and groundwater extraction. Regardless of the remedial alternative selected for Site OT 24, the downgradient extent of the BTEX plume needs to be more fully defined to ensure that the plume does not extend to the mangrove swamp, and to support the proper location of LTM and POC wells. Recommendations for additional plume definition are provided in Section 7.

6.3 BRIEF DESCRIPTION OF REMEDIAL ALTERNATIVES

This section describes how remedial technologies retained from the screening process were combined into three remedial alternatives for Site OT 24. Sufficient information on each remedial alternative is provided to facilitate a comparative analysis of effectiveness, implementability, and cost in Section 6.4.

6.3.1 Alternative 1--Intrinsic Remediation and Institutional Controls with Long-Term Groundwater Monitoring

Intrinsic remediation is achieved when natural attenuation mechanisms bring about a reduction in the total mass of a contaminant in the soil or dissolved in groundwater. Intrinsic remediation results from the integration of several subsurface attenuation mechanisms that are classified as either destructive or nondestructive. Destructive attenuation mechanisms include biodegradation, abiotic oxidation, and hydrolysis.

TABLE 6.2
INITIAL TECHNICAL IMPLEMENTABILITY SCREENING OF
TECHNOLOGIES AND PROCESS OPTIONS FOR GROUNDWATER REMEDIATION

SITE OT 24
 INTRINSIC REMEDIATION TS
 MACDILL AIR FORCE BASE, FLORIDA

General Response Action	Technology Type	Process Option	Implementability	Effectiveness	Relative Cost	Retain
Long-Term Monitoring	Periodic Groundwater Monitoring	Confirmation Wells	Some existing wells are available to confirm the progress of remediation. Sufficient space for additional wells between the source area and the mangrove swamp, if needed.	Necessary for all remediation strategies	Low	Yes
		Point-of-Compliance Wells	Sufficient distance exists between the plume and point-of-compliance to locate several wells.	Necessary to confirm model predictions	Low	Yes
Institutional Controls	Groundwater Use Control	Land Use Control/Regulate Well Permits	The plume lies within the Base boundary, and land and groundwater uses are under Base jurisdiction.	Necessary component of LTM program	Low	Yes
		Seal/Abandon Existing Wells	No production wells are known to exist in the current or predicted plume area.	Not required at this site	Low	No
		Point-of-Use Treatment	No shallow groundwater is extracted from the plume area for any use.	Poor	Moderate	No
		Meetings/Newsletters	Base public relations and environmental management offices have many information avenues to workers and residents.	Necessary	Low	Yes
Containment of Plume	Hydraulic Controls	Interceptor Trench Collection	Hydraulic conductivity of site soils favors pumping. Passive collection could feasibly be implemented, but relatively low dissolved BTEX concentrations indicate that this more aggressive remedial option is not necessary.	High	Moderate to High	No
		Minimum Pumping/Gradient Control	Hydraulic conductivities of site soils are moderate to high and would allow extraction of sufficient volumes. Treatment of extracrated water would probably be necessary. Plume unlikely to impact downgradient receptors.	Moderate	High	No
	Physical Controls	Slurry Walls/Grout Curtains	Limited effectiveness. Contaminated groundwater would seek alternate paths over, under, or around the walls.	Low to Moderate	High	No
		Sheet Piling	Limited effectiveness. Contaminated groundwater would seek alternate paths over, under, or around the walls.	Low to Moderate	High	No

TABLE 6.2 (Continued)
INITIAL TECHNICAL IMPLEMENTABILITY SCREENING OF
TECHNOLOGIES AND PROCESS OPTIONS FOR GROUNDWATER REMEDIATION

SITE OT 24

INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

General Response Action of Plume (cont.)	Technology Type	Process Option	Implementability	Effectiveness	Relative Cost	Retain
In Situ Groundwater Treatment	Reactive/Semi-Permeable Barriers	Biologically Active Zones	Degradation of BTEX can be stimulated by allowing groundwater to flow through a nutrient-rich barrier. New, unproven technology.	Moderate	High	No
	Biological	Oxygen and/or Nutrient Enhanced Biodegradation (Biosparging)	Differs from biologically active zone in that oxygen and/or nutrients are injected in or downgradient from plume to limit plume migration by enhancing biodegradation and reducing BTEX concentrations as the plume moves downgradient from the source area. Limited radius of influence and short-circuiting are common problems.	Low to moderate	Low	Yes
	Chemical/Physical	Intrinsic Remediation	A combination of natural biological, chemical, and physical removal mechanisms which occur to varying degrees on every site. Groundwater sampling at Site OT 24 indicates that this is an ongoing remediation process.	Moderate	Low	Yes
		Air Sparging (Volatilization)	Injection of air into contaminated aquifer creating a mass transfer of BTEX and CAHs into air bubbles and into vadose zone. Limited radius of influence and short-circuiting are common problems.	Low to moderate	Low	Yes
Aboveground Groundwater Treatment	Groundwater Extraction	Vertical Pumping Wells	A part of or the entire groundwater plume is pumped by installing wells with submersible pumps. Produces a large volume of water which requires additional treatment. Two inactive extraction wells and a treatment system are present, but may require repair.	Moderate	High	Yes
	Biological	Bioreactors	High flow rates require excessive retention times and large reactors. BTEX is often volatilized in these systems.	Moderate	High	No
	Chemical/Physical	Air Stripping	Cost-effective technology for removing varying concentrations of BTEX at higher flow rates. Air stripper present, but requires repair. Potential permitting for air emissions.	High	Moderate	Yes
		Activated Carbon UV/Ozone Reactors	Cost prohibitive for more concentrated BTEX. Creates a carbon disposal problem. High flow rates require excessive retention times and large, expensive reactors.	High Moderate	High (O&M) High	No No

TABLE 6.2 (Continued)
INITIAL TECHNICAL IMPLEMENTABILITY SCREENING OF
TECHNOLOGIES AND PROCESS OPTIONS FOR GROUNDWATER REMEDIATION

SITE OT 24

INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

General Response Action	Technology Type	Process Option	Implementability	Effectiveness	Relative Cost	Retain
Aboveground Groundwater Treatment (cont.)	Chemical/Physical (cont.)	Direct Discharge to Industrial Waste Water Treatment Plant (IWWTP)	Viable option when an IWWTP is readily available and capable of handling BTEX, TPH, CAHs, and hydraulic loading. IWWTP not available for this site.	High	High	No
		IWWTP	Viable option when an IWWTP is available and capable of handling BTEX, TPH, CAHs, and hydraulic loading. IWWTP is not available.	High	High	No
	Discharge to IWWTP or Sanitary Sewer	Sanitary Sewer	Viable option when access to sanitary sewer exists and hydraulic loading is acceptable. Sanitary sewer not readily available.	High	Low	No
		Vertical Injection Wells	Not recommended due to clogging and high maintenance.	Moderate	High	No
Source Removal/Soil Remediation	Treated Groundwater Reinjection	Injection Trenches	Require large trenches and can be subject to injection well permitting.	Moderate	High	No
		Storm Drains	Viable option. Generally requires discharge permit.	High	Low	Yes
		Landfilling	Excavation may be feasible at this site, but source removal could also be accomplished using less intrusive methods.	High	High	No
	Excavation/Treatment	Biological Landfarming	Excavation may be feasible at this site, but source removal could also be accomplished using less intrusive methods.	Moderate	Moderate	No
		Thermal Desorption	Excavation may be feasible at this site. Soil excavation not retained as a remedial option.	Moderate	High	No
		Bioventing	Air injection/extraction to increase soil oxygen levels and stimulate biodegradation of fuel residuals. Soils in source area should not limit effectiveness.	High	Low	Yes
	In Situ	Soil Vapor Extraction	Vapor extraction has been successfully implemented at other sites. Requires source definition and off-gas treatment. Bioventing is preferred, and relatively low BTEX and CAH concentrations indicate that vapor extraction is not necessary.	High	Moderate	No
		Soil Washing	Additional pore volumes of water and/or surfactant solution are forced through aquifer material to enhance the partitioning of hydrocarbons into the groundwater. Most effective in homogeneous sandy soils. Desired source removal could be more effectively performed using an alternate method such as bioventing.	Low	High	No

TABLE 6.2 (Concluded)
INITIAL TECHNICAL IMPLEMENTABILITY SCREENING OF
TECHNOLOGIES AND PROCESS OPTIONS FOR GROUNDWATER REMEDIATION

SITE OT 24
 INTRINSIC REMEDIATION TS
 MACDILL AIR FORCE BASE, FLORIDA

General Response Action	Technology Type	Process Option	Implementability	Effectiveness	Relative Cost	Retain
Source Removal/Soil Remediation (continued)	Mobile LNAPL Recovery	Dual-Pump Systems	Best suited for sites with >1 foot free product. Nonhomogeneous hydrogeology will limit effectiveness.	Moderate	High	No
		Skimmer Pumps/Bailers/Wicks	Best suited for sites with <1 foot free product. Water table depression not accomplished, limiting LNAPL recovery effectiveness.	Moderate	High	No
		Total Fluids Pumping	Best suited for sites with thin saturated zones where excessive groundwater will not be pumped. Pumps currently installed in existing recovery wells are total fluids pumps, and oil/water separator present at site.	Moderate	High	Yes
		Bioslurping	Combined vapor extraction, bioventing, and free product recovery system for remediation of soils and recovery of free-product. Most effective where depth to groundwater is less than 20 feet. Not justified by thin, localized LNAPL occurrence at Site OT 24.	Moderate to High	Moderate to High	No

Nondestructive attenuation mechanisms include sorption, dilution (caused by dispersion and infiltration) and volatilization. In some cases, intrinsic remediation will reduce dissolved contaminant concentrations below numerical concentration goals intended to be protective of human health and the environment. As indicated by the evidence of intrinsic remediation described in Section 4, these processes are occurring in the vicinity of Site OT 24 and will continue to reduce contaminant mass in the plume area.

Results of the Bioplume II model OT 24A suggest that the dissolved BTEX concentrations will decrease below the no-further-action guideline of 50 µg/L during simulation year 21 (calendar year 2016), and that the plume will not extend more than approximately 550 feet south of the EMTL. The model predicts that intrinsic remediation within the BTEX plume and along the plume margins will prevent further plume migration, and will cause a continual decrease in BTEX concentrations within the plume. The rate at which BTEX concentrations decrease is dependent on the assumed rate of decrease in the BTEX loading in the source area, described in Section 5.6.

Implementation of Alternative 1 would require the use of institutional controls such as land use restrictions and LTM. Land use restrictions may include placing long-term restrictions on soil excavation in the source area and long-term restrictions on groundwater well installations within and downgradient of the plume area. The intent of these restrictions would be to reduce potential receptor exposure to contaminants by legally restricting activities within areas affected by site-related contamination.

At a minimum, groundwater monitoring within the plume area would be conducted periodically as part of the implementation of this remedial alternative to evaluate the progress of natural attenuation processes and to verify the accuracy of model predictions. Based on the potential plume migration suggested by the modeling, it is unlikely that benzene concentrations exceeding the most stringent Florida standard of 1 µg/L (FDEP, 1994) would be present at the upgradient (northern) edge of the mangrove swamp. This would be true even if it were assumed that simulated contaminant concentrations consist entirely of benzene rather than a mixture of the BTEX compounds. In addition, field data suggest that it is unlikely that vinyl chloride concentrations exceeding the Florida standard of 1 µg/L (FDER, 1989) would be present in groundwater at the mangrove swamp. It is unlikely that benzene and dissolved BTEX concentrations exceeding the no-further-action guideline of 50 µg/L (Table 6.1) would be present more than approximately 500 feet downgradient from the EMTL. The recommended components of LTM, including well locations, are described in Section 7.2.

Public education on the selected alternative would be developed to inform Base personnel and residents of the scientific principles underlying source reduction and intrinsic remediation. This education could be accomplished through public meetings, presentations, press releases, and posting of signs where appropriate. Periodic site reviews also could be conducted using data collected during the LTM program. The purpose of these reviews would be to evaluate the extent of contamination, assess contaminant migration and attenuation through time, document the effectiveness of

source removal and/or institutional controls at the site, and reevaluate the need for additional remedial actions at the site.

6.3.2 Alternative 2--Bioventing/Biosparging in Source Area, Intrinsic Remediation, and Institutional Controls with Long-Term Groundwater Monitoring

Available data indicate that the mobile LNAPL layer at Site OT 24 is thin and very localized. Therefore, recovery of the product itself would probably not be cost effective, and would most likely be technically difficult to achieve. A better approach would be to allow the product to smear across the soil column as the water table rises and falls, and to remediate the small quantity of resulting residual LNAPL by bioventing and/or biosparging techniques. This alternative is identical to Alternative 1 except that bioventing and/or biosparging would be used to enhance the biodegradation of organic contaminants in subsurface soils by supplying oxygen to indigenous microbes using low-flow air injection in the vicinity of Site OT 24. Bioventing is preferred over soil vapor extraction (SVE) because bioventing uses a low rate of air injection that significantly reduces emissions into the atmosphere while maximizing *in situ* biodegradation. Due to the relatively low volatile content of the mobile and residual LNAPL present in the subsurface at the site, the use of SVE to remove potentially combustible vapors prior to implementation of bioventing is judged to be unnecessary.

Bioventing is not a proven technology in the remediation of chlorinated-solvent-contaminated soils. However, the relatively low magnitude of CAH concentrations detected in the groundwater indicate that substantial amounts of solvent compounds are not present in the vadose zone.

On the basis of Parsons ES experience in the application of bioventing technology in shallow Florida soils, one horizontal air injection well installed within the area of maximum dissolved BTEX concentrations and estimated mobile LNAPL occurrence should be sufficient to remediate the most significant contamination in the vicinity of Site OT 24. The length of the well would be approximately 20 feet. Approximately four shallow vapor monitoring points also would be installed to allow measurement of the effectiveness of the injection well.

Based "on" other bioventing systems operating in Florida soils, a bioventing/biosparging system should remove at least 95 percent of residual soil BTEX compounds within 3 to 4 years (Parsons ES, 1995e). If bioventing alone is used, then selective operation of the system during several dry periods (when water levels are low) should substantially decrease residual BTEX concentrations in the capillary fringe and below the average water table. The effect of this relatively rapid source removal on the migration of the groundwater BTEX plume was evaluated using the Bioplume II model OT 24B, as described in Section 5.6.2. The simulation OT 24B assumes that a decrease in soil concentrations due to bioventing will produce a similar decrease in BTEX dissolution into the groundwater. The results of this model suggest that remediation of source area soils would promote a more rapid decrease in dissolved BTEX concentrations. After approximately 17 years, the maximum dissolved BTEX concentrations would drop below 50 µg/L.

An alternative design option would be to inject air below the groundwater surface and allow the air (oxygen) to move upward through the capillary fringe and into the contaminated vadose zone. This process, known as air sparging or biosparging, also would increase the DO content of the groundwater and promote more rapid degradation of dissolved BTEX compounds and CAHs in the plume. Installation of the horizontal air injection well very near the average groundwater surface would allow it to function as a sparging well during periods of relatively high water levels when the well would be submerged, and as a bioventing well during periods of low water levels. This configuration would promote biodegradation of residual BTEX both above and below the groundwater surface, and seasonally promote aerobic biodegradation of dissolved BTEX compounds by increasing the DO content of the groundwater. As described in Section 5.6.2, the model results suggest that the time to site closure may not be significantly decreased if a bioventing/biosparging system is installed and operated as opposed to a bioventing system.

As with Alternative 1, institutional controls and LTM would be required. POC and LTM wells would be installed in the locations indicated in Section 7.2. At a minimum, groundwater monitoring would be conducted annually as part of this remedial alternative to evaluate the progress of source removal and natural attenuation processes.

6.3.3 Alternative 3--Groundwater Extraction, Bioventing/Biosparging in Source Area, Intrinsic Remediation, and Institutional Controls with Long-Term Groundwater Monitoring

This option would include the scenarios described for Alternatives 1 and 2 above, but also would include groundwater pumping in the most concentrated area of the plume. The objective of the pumping would be to reduce dissolved benzene and total BTEX concentrations in the source area to below 500 µg/L and 1,000 µg/L, respectively, which are the levels that could trigger a "monitoring only" status for the site (Table 6.1). Any remaining dissolved contaminant mass would be allowed to naturally attenuate. Groundwater pumping in the source area would temporarily depress groundwater levels and allow the bioventing system to oxygenate the newly exposed interval, resulting in more effective remediation of residual LNAPL in source area soils. The extracted groundwater could be treated onsite in the currently inactive treatment system installed by CH2M Hill (1991b) and discharged to the drainage ditch located immediately north of the site. Volatile chlorinated solvents and solvent byproducts (e.g., vinyl chloride) present in the extracted groundwater also would be removed during the treatment process.

6.4 EVALUATION OF ALTERNATIVES

This section provides a comparative analysis of each of the remedial alternatives based on the effectiveness, implementability, and cost criteria. A summary of this evaluation is presented in Section 6.5.

6.4.1 Alternative 1--Intrinsic Remediation and Institutional Controls with Long-Term Groundwater Monitoring.

6.4.1.1 Effectiveness

Alternative 1 is based on the effectiveness of natural processes that minimize contaminant migration and reduce contaminant mass over time, and the effectiveness of institutional controls. Section 5 of this document presents the results of the Bioplume II modeling completed to support the intrinsic remediation alternative at Site OT 24. Model OT 24A results predict that natural attenuation mechanisms will significantly limit contaminant migration and reduce contaminant mass and toxicity. The Bioplume II model is based upon reasonably conservative assumptions, as described in Section 5.7. Groundwater monitoring at the LTM and POC wells would ensure the protectiveness of this alternative. While this alternative would not cease to be protective if the BTEX plume is intercepted at the POC wells, such an instance would indicate that site conditions should be reevaluated. Prior to a final decision to implement this alternative, the downgradient extent of the BTEX plume should be more fully defined to ensure that contaminated groundwater is not discharging to surface water in the mangrove swamp, and to allow the plume to be monitored over time.

The effectiveness of this remedial alternative requires that excavations or drilling within the source area be conducted only by properly protected site workers. Reasonable land use assumptions for the plume area indicate that receptor exposure is unlikely unless excavation or drilling activities bring saturated soil to the surface. Long-term land use restrictions would be required to ensure that shallow groundwater will not be pumped or removed for potable use in the vicinity of the plume (at a minimum within the area between the EMTL and the downgradient drainage channel). Existing health and safety plans should be enforced to reduce risks from additional excavation or from installing and monitoring additional POC wells.

Compliance with program goals is one component of the long-term effectiveness evaluation criterion. Alternative 1 would satisfy program objectives designed to promote intrinsic remediation as a component of site remediation and to scientifically document naturally occurring processes. This alternative also satisfies program goals for cost effectiveness and waste minimization. Apart from the administrative concerns associated with enforcement of long-term land use restrictions and a long-term groundwater monitoring program, this remedial alternative should provide reliable, continued protection.

6.4.1.2 Implementability

Alternative 1 is not technically difficult to implement. Installation of LTM and POC wells and periodic groundwater sampling and analysis are standard procedures. However, some logistical challenges would be posed by the need to better define the downgradient extent of the plume and install LTM wells in the dense forest. Corridors would either have to be cleared by hand or using mechanical equipment to allow access to the desired sampling locations, and the access paths would need to be maintained through time to allow for periodic monitoring. Long-term management efforts would be required to ensure that proper sampling procedures are followed. Periodic site

reviews should be conducted to confirm the adequacy and completeness of LTM data and to verify the effectiveness of this remediation approach. There also may be administrative concerns associated with long-term enforcement of groundwater use restrictions. Future land use within the source area may be impacted by leaving contaminated soil and groundwater in place. Regulators and the public would have to be informed of the benefits and limitations of the intrinsic remediation option, but educational programs are not difficult to implement.

6.4.1.3 Cost

The cost of Alternative 1 is summarized in Table 6.3. It is assumed for cost comparison purposes that dissolved benzene concentrations would exceed state guidelines throughout the plume for approximately 21 years under Alternative 1, and that sampling would be performed annually for 10 years, followed by eight biannual sampling events (total LTM period of 26 years) to demonstrate that intrinsic remediation has uniformly reduced BTEX and vinyl chloride concentrations to below applicable guidelines. Capital costs include the following elements:

- Construction of four new plume definition wells and collection of groundwater samples for BTEX and CAH analysis from a total of six wells prior to final selection of LTM and POC well locations. The new wells would be installed in the forested area, and would consist of manually-driven, stainless steel wellpoints. The sampled wells would include existing temporary wellpoints 24PZ-1S and 24PZ-3S and the four new wells.
- Construction of three new LTM wells and three new POC wells. The continued use of one of the new plume definition wells as an LTM well is assumed. Two of the new LTM wells would replace the existing temporary monitoring points 24MP-1S and 24PZ-1S, and the third LTM well would replace existing monitoring well MD24-4, which is screened too deep to adequately monitor for BTEX. It is assumed that the replacement for 24PZ-1S, which is located in the forest, will consist of a manually-driven stainless steel wellpoint due to access difficulties. As described in Section 7, the new wellpoint would have a surface seal, PVC riser pipe, and protective casing (features that are not incorporated in 24PZ-1S) to enhance the representativeness of groundwater samples. The remaining two new LTM wells would be conventionally constructed using a truck-mounted drilling rig.

Included in the \$250,770 total present worth cost estimate for Alternative 1 are the costs of maintaining institutional controls and long-term groundwater monitoring for a total of 26 years. Cost calculations are contained in Appendix F.

TABLE 6.3
ALTERNATIVE 1 - COST ESTIMATE
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

<u>Capital Costs</u>	<u>Cost</u>
Design/construct four plume definition wells, three LTM wells, and three POC Wells. Initial sampling of six wells for BTEX and CAHs.	\$14,970
<u>Operation, Maintenance, and Monitoring Costs (Annual)</u>	<u>Annual Cost</u>
Conduct Annual Groundwater Monitoring of 8 wells for 10 years, followed by 8 biannual monitoring events ^{a/}	\$8,235
Maintain Institutional Controls/Public Education (25 years)	\$5,000
Project Management and Reporting (25 years)	\$10,175
<u>Present Worth of Alternative 1 ^{a/}</u>	<u>\$250,770</u>

^{a/} Based on an annual inflation (discount) factor of 7 percent (USEPA, 1993).

Note: Costs assume that well installation and LTM are performed by Tampa-area personnel.

6.4.2 Alternative 2 - Bioventing/Biosparging in Source Area, Intrinsic Remediation, and Institutional Controls with Long-Term Groundwater Monitoring

6.4.2.1 Effectiveness

The effectiveness of the intrinsic remediation, institutional controls, and LTM components of this alternative are as described for Alternative 1. Bioventing is an established technology that effectively remediates fuel hydrocarbons in the unsaturated zone via the addition of oxygen to stimulate biodegradation by naturally-occurring microorganisms. The application of bioventing for 1 year at the Patrick AFB, Florida BX gasoline station resulted in a 95-percent reduction in the total BTEX residuals in soil impacting groundwater (Parsons ES, 1995e). Given the Bioplume II model OT 24B results discussed in Section 5.6, reduction in the mass of BTEX compounds that dissolve into groundwater should speed site closure. Installation of a combination bioventing/biosparging system, as described in Section 6.3.2, may result in more effective remediation of residual LNAPL below the average groundwater surface. As with Alternative 1, this alternative would require long-term land use restrictions, as well as enforcement of health and safety plans to reduce risks to workers during installation of the bioventing/biosparging system and installation and monitoring of LTM and POC wells. The rapid reduction in soil BTEX levels would reduce the long-term risk to any Base workers who might be required to excavate in this area.

Alternative 2 should provide reliable, continuous protection with little risk from temporary system failures. This alternative also complies with the program goals because intrinsic remediation remains the predominant remedial method for fuel hydrocarbons dissolved in groundwater at the site. However, this remedial alternative may result in the generation of 5 to 10 cubic yards of potentially contaminated soil requiring treatment and/or disposal, unless the Base is allowed to use these soils as backfill material in the excavated vent well and utility trenches.

It is assumed that dissolved benzene and total BTEX concentrations will exceed applicable state guidelines for no further action (Table 6.1) throughout the plume for approximately 17 years under Alternative 2. An additional 5 years of groundwater monitoring is recommended to ensure that intrinsic remediation has uniformly reduced all BTEX and CAH compounds to levels below state guidelines.

6.4.2.2 Implementability

Installing and operating a bioventing/biosparging system to reduce source area BTEX concentrations at Site OT 24 could present additional implementability concerns. Installation would involve shallow trench excavation for well installation, piping, and manifold connections, and care would have to be taken to avoid damaging existing subsurface utilities related to the extraction well system present at the site. However, the grassy area immediately south of the EMTL is not currently used in Base operations, and disruption of regular site activities would probably be relatively insignificant. Bioventing/biosparging equipment is readily available, and the technology used to construct such systems is proven and reliable. Installation and operation of a full-scale bioventing/biosparging system would require an increased

commitment of labor-hours and other resources to maintain and monitor the system. If high chlorinated solvent concentrations are detected in extracted soil gas during system installation, it may be advisable to operate the system in an SVE mode in order to remediate residual chlorinated solvents more rapidly. However, the low magnitude of CAH concentrations detected in the groundwater indicate that substantial solvent concentrations are not present in vadose zone soils.

The technical and administrative implementability concerns associated with the intrinsic remediation and LTM component of this remedial alternative are similar to those discussed in Alternative 1. Public acceptance of this alternative may be more positive than Alternative 1 because source removal actions would be implemented.

6.4.2.3 Cost

The estimated capital and operating costs of Alternative 2 are shown in Table 6.4. The total present worth cost of Alternative 2 is approximately \$358,551. The cost of Alternative 2 is greater than Alternative 1 because of the addition of the bioventing/biosparging system, even though the length of LTM is reduced from 26 to 22 years. It is assumed that the bioventing/biosparging system would be operated for 4 years after installation. Annual LTM would continue for a total of 10 years, followed by 12 years of biannual monitoring to ensure that intrinsic remediation is reducing BTEX concentrations below state G-II groundwater requirements (Table 6.1) throughout the plume, and to verify that contamination above these requirements does not reach the POC wells.

6.4.3 Alternative 3--Groundwater Extraction, Bioventing/Biosparging in Source Area, Intrinsic Remediation, and Institutional Controls with Long-Term Groundwater Monitoring

6.4.3.1 Effectiveness

This alternative is identical to Alternative 2, with the addition of limited groundwater extraction in the contamination source area. The effectiveness of bioventing, intrinsic remediation, institutional controls, and LTM were described in Section 6.4.2. Groundwater extraction is an established technology for reducing source contamination and controlling plume migration. The goal of groundwater extraction would be to target the removal of the highest dissolved BTEX and CAH concentrations so that intrinsic remediation of contaminants beyond the source area could proceed without the introduction of additional contaminant mass. The model OT 24C suggests that reduction of the source by bioventing/biosparging and groundwater extraction would expedite the decrease in the size of the BTEX plume.

The easternmost of the two groundwater extraction wells installed by CH2M Hill (1991b) would be refurbished as necessary and used to pump groundwater and mobile LNAPL. This is the most contaminated area of the site, and appears to be the primary source of BTEX that is migrating downgradient. The resulting influx of clean groundwater would accelerate the partitioning of BTEX from saturated soils. Simple batch-flushing calculations (Appendix D) and the results of model OT 24C suggest that this pumping should reduce source area dissolved BTEX levels to below the threshold

TABLE 6.4
ALTERNATIVE 2 - COST ESTIMATE
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

<u>Capital Costs</u>	<u>Cost</u>
Design/construct four plume definition wells, three LTM wells, and three POC wells. Initial sampling of six wells for BTEX and CAHs.	\$14,970
Design/Construct Bioventing/Biosparging System, Including Manifolding and Blowers (assuming one horizontal well 20 feet long plus 100 feet to an electricity source)	\$46,500
<u>Operation, Maintenance and Monitoring Costs (Annual)</u>	<u>Annual Cost</u>
Operate and Maintain Bioventing/Biosparging System + Effectiveness Testing and Reporting (4 years)	\$21,435
Conduct Annual Groundwater Monitoring of 8 wells for 10 years, followed by 6 Biannual Monitoring Events ^{a/}	\$8,235
Maintain Institutional Controls/Public Education (21 years)	\$5,000
Project Management and Reporting (21 years)	\$10,175
<u>Present Worth of Alternative 2 ^{a/}</u>	<u>\$358,551</u>

^{a/} Based on an annual discount factor of 7 percent (USEPA, 1993).

levels for "monitoring only" (1,000 µg/L total BTEX and 500 µg/L benzene per Table 6.1) within approximately 2 years.

Extracted groundwater would likely require treatment prior to discharge. The oil/water separator installed by CH2M Hill (1991b) could be used to separate groundwater and free product, and the onsite air stripper could be used to treat the groundwater. Discharge of treated groundwater to the Base perimeter drainage ditch located north of the site would likely require acquisition of a National Pollutant Discharge Elimination System (NPDES) permit, and effluent quality monitoring would have to be performed periodically at the discharge point.

Alternative 3 should provide reliable, continuous protection with little risk from temporary system failures. This alternative also complies with program goals because intrinsic remediation remains an important remediation method for the site. However, this remedial alternative will result in the generation of groundwater and other wastes requiring treatment and/or disposal.

It is assumed that dissolved benzene and total BTEX concentrations will exceed applicable state guidelines for no further action (Table 6.1) for approximately 13 years under Alternative 3. It is recommended that groundwater sampling proceed for an additional five years to demonstrate that intrinsic remediation has uniformly reduced all BTEX and chlorinated solvent concentrations to levels below state guidelines, resulting in a total of 18 years of LTM.

6.4.3.2 Implementability

The technical and administrative implementability concerns associated with the bioventing/biosparging, intrinsic remediation, and LTM components of this remedial alternative are similar to those discussed for Alternatives 1 and 2 (Sections 6.4.1.2 and 6.4.2.2). Implementability concerns associated with the operation of a groundwater extraction system primarily revolve around the quality and operability of the existing groundwater extraction and treatment system. The system has reportedly been scavenged to provide parts and equipment for other extraction systems operating at the Base; the amount of work and new equipment needed to refurbish the existing system is not known. Repair and operation of a groundwater extraction system would require a significant commitment of man-hours and other resources to maintain and monitor the system. In addition, the FDEP would have to issue air emissions and NPDES permits to allow treatment and disposal of the treated groundwater.

6.4.3.3 Cost

The estimated capital and operating costs of Alternative 3 are shown in Table 6.5. The total present worth cost of Alternative 3 is \$417,225. The cost of Alternative 3 is increased from the costs of Alternative 2 by the addition of groundwater/free product extraction and treatment. The cost for repair/refurbishment of the existing extraction and treatment system is not known; therefore the \$20,000 cost for this item in the table is speculative. It is assumed that the bioventing/biosparging system would operate for 3 years after installation, and the groundwater extraction system would operate for 2 years after installation. LTM would continue annually for 17 years and biannually for

TABLE 6.5
ALTERNATIVE 3 - COST ESTIMATE
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

<u>Capital Costs</u>	<u>Cost</u>
Design/construct four plume definition wells, three LTM wells, and three POC wells. Initial sampling of six wells for BTEX and CAHs	\$14,970
Repair Groundwater Extraction and Treatment System.	\$20,000
Design/Construct Bioventing/Biosparging System	\$46,500
Water Discharge Permitting	\$5,000
Air Emissions Permitting	\$5,000
<u>Operation, Maintenance and Monitoring Costs (Annual)</u>	<u>Annual Cost</u>
Operate and Maintain Groundwater Extraction/Treatment Systems (2 years)	\$20,640
Quarterly Groundwater Extraction System Performance Reports (2 years)	\$5,600
Air Stripper Maintenance	\$7,000
Operate and Maintain Bioventing/Biosparging System and Effectiveness Testing and Reporting (3 years)	\$21,435
Conduct Annual Groundwater Monitoring at 8 wells for 10 years, followed by Four Biannual Sampling Events	\$8,235
Maintain Institutional Controls/Public Education (17 years)	\$5,000
Project Management and Reporting (17 years)	\$10,175
<u>Present Worth of Alternative 2 ^{a/}</u>	<u>\$417,225</u>

^{a/} Based on an annual discount factor of 7 percent (USEPA, 1993).

Note: Costs assume that LTM and bioventing/groundwater extraction system maintenance are performed by Tampa-area personnel.

8 years after bioventing system shutdown to ensure that intrinsic remediation is reducing remaining BTEX concentrations below regulatory criteria throughout the plume and to verify that excessive contamination does not reach the POC wells or the downgradient mangrove swamp.

6.5 RECOMMENDED REMEDIAL APPROACH

Three alternatives have been evaluated for remediation of the shallow groundwater at Site OT 24. Components of the alternatives evaluated include groundwater/product extraction and treatment, bioventing/biosparging, intrinsic remediation with LTM, and institutional controls. Table 6.6 summarizes the results of the evaluation based upon effectiveness, implementability, and cost criteria.

Alternative 1 makes maximum use of intrinsic remediation mechanisms to reduce plume migration and toxicity. Alternatives 2 and 3 would provide additional protection against further plume migration by reducing the magnitude of continuing sources while still relying on intrinsic remediation mechanisms to reduce plume mass and toxicity in the groundwater. Implementation of Alternatives 2 or 3 would decrease the time frame for remediation, but would require a greater capital expenditure.

Each of the remedial alternatives are implementable, and each of them would effectively reduce potential hydrocarbon migration and toxicity. Each of the alternatives should be acceptable to the public and regulatory agencies because they are protective of human health and the environment and reduce soil and groundwater contamination to below cleanup guidelines. Implementation of any of the alternatives will require land use and groundwater use controls to be enforced for an estimated 18 to 26 years, depending on the alternative selected and its effectiveness. Groundwater monitoring would be required for the same period.

On the basis of this evaluation, the Air Force recommends Alternative 1 as achieving the best combination of risk reduction and cost effectiveness. The final evaluation criterion used to compare each of the two remedial alternatives was cost. It is the opinion of the Air Force that the additional cost of Alternatives 2 and 3 over Alternative 1 is not justified by the estimated 4- to 8-year decrease in remediation time resulting from the implementation of source removal and/or groundwater extraction activities. In addition, it is possible that actual biodegradation rates will be more rapid than portrayed by model OT 24A, which incorporates a number of conservative elements. The low magnitude of chlorinated solvent and solvent byproduct concentrations detected in the groundwater, and the evidence that reductive dehalogenation of dissolved solvents is occurring, suggest that Alternative 1 is also appropriate for these compounds. However, Alternatives 2 or 3 (bioventing/biosparging with or without groundwater/product extraction as described in Sections 6.3.2 and 6.3.3) should be considered as a contingency in the event that any of the following events occur:

- land use in this area changes to commercial or residential;
- measured BTEX reductions in the groundwater are substantially slower than predicted by the Bioplume II model; or

TABLE 6.6
SUMMARY OF REMEDIAL ALTERNATIVES EVALUATION
GROUNDWATER REMEDIATION
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Remedial Alternative	Effectiveness	Implementability	Present Worth Cost Estimate
Alternative 1 - Intrinsic Remediation - Long-Term Monitoring - Institutional Controls	Contaminant mass, volume, and toxicity will be significantly reduced and plume migration should be halted. Groundwater quality guidelines for BTEX not likely to be exceeded at POC wells.	Readily implementable. Long-term management, groundwater use controls, and monitoring required for an estimated maximum of 26 years. Minimal exposure of site workers if excavation is carefully controlled in source area. If water quality guidelines are exceeded at POC wells, additional remedial work may be required.	\$250,770
Alternative 2 - Bioventing/Biosparging - Intrinsic Remediation - Long-Term Monitoring - Institutional Controls	Similar to Alternative 1, with the addition of a bioventing system (with or without biosparging) to address residual LNAPL in soil. Contaminant mass, volume, and toxicity will be reduced more rapidly than in Alternative 1. Less likely that groundwater quality guidelines will be exceeded at POC wells.	Readily implementable. Installation of a bioventing/biosparging system should pose no problems. Bioventing/biosparging estimated to continue for 4 years. Long-term site management, groundwater controls, and monitoring required for an estimated maximum of 22 years. If water quality standards are exceeded at POC wells, additional remedial work may be required.	\$358,551
Alternative 3 - Groundwater Extraction - Bioventing/Biosparging - Intrinsic Remediation - Long-Term Monitoring - Institutional Controls	Similar to Alternative 2, with the addition of a groundwater extraction system to remove dissolved BTEX in groundwater. Contaminant mass, volume, and toxicity will be reduced more rapidly than in Alternatives 1 and 2. Less likely that groundwater quality guidelines will be exceeded at POC wells compared to Alternatives 1 and 2.	Readily implementable, but would require repair/refurbishment of existing extraction and treatment system. Bioventing estimated to continue for 3 years; groundwater extraction estimated to continue for 2 years. Long-term management, groundwater controls, and monitoring required for an estimated maximum of 18 years. If water quality standards are exceeded at POC wells, additional remedial work may be required.	\$417,225

- it is determined that significant CAH (e.g., vinyl chloride) or BTEX concentrations have migrated to or near a potential discharge area such as the mangrove swamp.

SECTION 7

LONG-TERM MONITORING PLAN

7.1 OVERVIEW

In keeping with the requirements of the preferred remedial alternative for Site OT 24 (intrinsic remediation with LTM), a long-term groundwater monitoring plan was developed. The purpose of this component of the preferred remedial alternative for the site is to assess site conditions over time, confirm the effectiveness of naturally occurring processes at reducing contaminant mass and minimizing contaminant migration, and evaluate the need for additional remediation.

The LTM plan consists of identifying the locations of two separate groundwater monitoring networks and developing a groundwater sampling and analysis strategy to demonstrate attainment of site-specific remediation goals (Table 6.1) and to verify the predictions of the Bioplume II model. The strategy described in this section is designed to monitor plume migration over time and to verify that intrinsic remediation is occurring at rates sufficient to protect potential receptors. In the event that data collected under this LTM program indicate that naturally occurring processes are insufficient to protect human health and the environment, contingency controls to augment the beneficial effects of intrinsic remediation would be necessary.

As described in Section 6.2.4, the downgradient extent of the BTEX plume should be more fully defined prior to finalization of the LTM plan. Prior to finalization of additional monitoring well locations, performance of a groundwater elevation measurement round that incorporates all available water level monitoring stations in the area (including wells installed at the adjacent POL fuel farm) is recommended to provide a more widespread, comprehensive "snapshot" of the water table configuration and groundwater flow directions. Based on currently available data, four monitoring wells should be installed in the forested area that, along with existing monitoring point 24PZ-3S, will form an east/west-line of monitoring stations across the BTEX plume near the estimated downgradient toe of the plume. The proposed well locations are shown on Figure 7.1. Groundwater quality samples and groundwater elevation data should be collected from monitoring points 24PZ-1S, 24PZ-3S, and the four new wells prior to installation of POC wells to better establish the downgradient extent of the plume and contaminant migration directions. It is recommended that the new wells consist of manually driven stainless-steel wellpoints screened within the uppermost 5 feet of the surficial aquifer. In this way, the wells can be installed with a minimum of disturbance to the forest environment, which may include jurisdictional wetland areas. Once the well screens are in place, the soil around the riser pipe should be excavated to a depth of 18 inches, and a 6-inch bentonite seal followed by a 1-foot grout seal should be emplaced to ensure that water quality samples are not affected by surface recharge.

A steel protective casing and a concrete pad should be installed at the ground surface to protect the well and prevent ponding of precipitation above the well. Following plume definition, selected plume definition wells can be used as LTM wells as described below.

7.2 MONITORING NETWORKS

Two separate sets of wells will be utilized at the site as part of the intrinsic remediation with LTM remedial alternative. The first set will consist of five existing and proposed LTM wells within and upgradient from the observed BTEX plume to verify the results of the Bioplume II modeling effort and to ensure that natural attenuation is occurring at rates sufficient to minimize plume expansion (i.e., meet the G-II level of numerical groundwater remediation goals for the site).

The second set will include POC groundwater monitoring wells to be located along a line perpendicular to the direction of groundwater flow near the northern edge of the mangrove swamp. The purpose of these POC wells is to verify that no BTEX or CAH compounds exceeding state groundwater quality guidelines discharge to the swamp and impact surface water quality. Model results suggest that the plume front will not reach these POC locations. This network will consist of three new shallow groundwater monitoring wells screened within the upper 5 to 8 feet of the shallow aquifer.

The LTM and POC well locations are shown on Figure 7.1. The POC well locations are preliminary because the groundwater flow and contaminant migration direction within the forested area south of monitoring point 24PZ-1S is not well established. Once four additional wells are installed in the forest and sampled to better define the downgradient extent of the BTEX plume, groundwater quality and water table elevation data should be used to determine the contaminant migration direction and to select the optimum POC well locations.

7.2.1 Long-Term Monitoring Wells

A maximum of five groundwater monitoring wells within and upgradient from the existing BTEX contaminant plume will be used to monitor the effectiveness of intrinsic remediation in reducing total contaminant mass and minimizing contaminant migration at Site OT 24. The LTM network will supplement the POC wells to provide early confirmation of model predictions and to allow additional response time if necessary.

This LTM network will consist of wells screened in the shallow portion of the surficial aquifer because this is where the dissolved BTEX plume appears to be migrating. One LTM well should be installed upgradient from the existing plume, near existing well MD24-4 (Figure 7.1). Well MD24-4 is screened from 10 to 20 feet bgs, and the newly installed LTM well should be screened in the uppermost 8 feet of the surficial aquifer (screen interval of approximately 2 to 12 feet bgs). The remaining four LTM wells are located along the plume axis, including a new well adjacent to 24MP-1, MD24-6, a new well adjacent to 24PZ-1S, and one of the new monitoring wells proposed to better define the downgradient extent of the BTEX plume (Figure 7.1). This LTM plan assumes that monitoring points 24MP-1S and 24PZ-1S will be replaced with more conventionally constructed monitoring wells for LTM purposes. The replacement for 24PZ-1S, which is located within the forested area, could consist

of a manually-driven stainless steel wellpoint with a surface seal, protective casing, and concrete pad, as described for the proposed plume definition wells in Section 7.1. Although use of a steel riser pipe will be required to drive the wellpoint to the desired depth, this riser pipe should be replaced with a more inert PVC pipe to prolong the well life. The wellpoint screen should be 3 to 5 feet long, and should be placed within the top 5 feet of the saturated zone.

7.2.2 Point-of-Compliance Wells

Once the downgradient extent of the BTEX plume and the groundwater flow direction within the forest have been established, three POC monitoring wells should be installed along an east/west line near the upgradient (north) edge of the mangrove swamp (Figure 7.1). The purpose of the POC wells is to verify that no contaminated groundwater exceeding state guidelines for G-II groundwater (Table 6.1) at petroleum-contaminated sites migrates beyond the area under institutional control. An additional objective is to ensure that significant concentrations of BTEX or (CAHs) do not discharge to surface water either in the swamp or the drainage channel bordering the swamp on the south. Model results suggest that the contaminant plume will not migrate beyond the POCs at concentrations exceeding applicable guidelines, and these POC wells are the technical mechanisms used to demonstrate protection of human health and the environment and compliance with site-specific numerical remediation goals. These wells will be installed and monitored to ensure that the selected remedy is providing the anticipated level of contaminant reduction and remediation at the site.

The POC wells should be located as close to the mangrove swamp as possible. A narrow band of laurel oak is present along the northern edge of the mangrove swamp. These trees are likely located on spoil placed during historic excavation activity. If it is not practical to install the POC wells within or south of the oak grove, then they should be installed along the northern edge of the oaks, at the approximate locations shown on Figure 7.1. This LTM plan assumes that, because the mangrove swamp and nearby drainage channel are probable groundwater discharge areas, downward hydraulic gradients would not be prominent at these locations, and BTEX contamination would be in the shallow portion of the surficial aquifer. Consequently, the POC wells should be screened within the uppermost 5 to 8 feet of the surficial aquifer. Similar to the LTM wells located in the forest, the POC wells located in the forest could consist of manually driven wellpoints with a surface seal, concrete pad, and protective casing to minimize disruption of the forest ecosystem.

7.3 GROUNDWATER SAMPLING

To ensure that contaminant removal occurring at Site OT 24 is sufficient to protect human health and the environment and meet site-specific remediation goals, the long-term groundwater monitoring plan includes a comprehensive sampling and analysis plan (SAP). LTM and POC wells will be sampled and analyzed annually to verify that naturally occurring processes are effectively reducing contaminant mass and mobility. Reductions in toxicity will be implied by mass reduction. The SAP also will be aimed at assuring intrinsic remediation can achieve site-specific remediation BTEX and CAH concentration goals that are intended to be protective of human health and the environment.

7.3.1 Analytical Protocol

All LTM and POC wells in the LTM program will be sampled and analyzed to determine compliance with chemical-specific remediation goals and to verify the effectiveness of intrinsic remediation at the site. Groundwater level measurements will be made during each sampling event. Groundwater samples from LTM and POC wells will be analyzed for the parameters listed in Tables 7.1 and 7.2, respectively. A site-specific SAP should be prepared as part of a remedial action plan (in compliance with state requirements) prior to initiating the LTM program.

7.3.2 Sampling Frequency

The LTM costs presented in Section 6 assume that each of the LTM and POC sampling points will be sampled annually for a period of 10 years, followed by 16 years of biannual sampling. This scenario is based on the assumption that the plume will be determined to be either receding or at steady state within the initial 10 years of LTM. The LTM plan should be periodically reviewed and revised as appropriate on the basis of available groundwater quality data. For example, if the sampling indicates that the BTEX plume is receding and no longer presents a threat to the surface water bodies in the drainage channel and the mangrove wetlands, then continued monitoring of the POC wells may not be required. In addition, if the data collected during this time period support the anticipated effectiveness of the intrinsic remediation alternative at this site, the sampling frequency can be reduced, or sampling can be eliminated. If the data collected at any time during the monitoring period indicate the need for additional remedial activities at the site, sampling frequency should be adjusted accordingly.

TABLE 7.1
LONG-TERM GROUNDWATER MONITORING ANALYTICAL PROTOCOL
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Analyte	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Ferrous Iron (Fe ²⁺)	Colorimetric A3500-Fe D	Field only.	Elevated ferrous iron concentrations may be indicative of the anaerobic biodegradation process of iron reduction.	Every year for 10 years, and every other year for 16 years.	Collect 100 milliliters (mL) of water in a glass container; acidify with hydrochloric acid per method.	Field
Ferrous Iron (Fe ²⁺)	Colorimetric Hach 25140-25	Alternate method; field only.	Same as above.	Every year for 10 years, and every other year for 16 years.	Collect 100 mL of water in a glass container.	Field
Temperature	E170.1	Field only.	Metabolism rates for microorganisms depend on temperature.	Every year for 10 years, and every other year for 16 years.	N/A	Field
Dissolved Oxygen	Dissolved oxygen meter	Refer to Method A4500 for a comparable laboratory procedure.	The oxygen concentration is a data input to the Bioplume II model; concentrations less than 1 mg/L generally indicate an anaerobic pathway.	Every year for 10 years, and every other year for 16 years.	Collect 300 mL of water in biochemical oxygen demand bottles; analyze immediately; alternately, measure dissolved oxygen in situ.	Field
pH	E150.1/SW9040, direct reading meter	Protocol/Handbook methods ^{a/} .	Aerobic and anaerobic processes are pH-sensitive.	Every year for 10 years, and every other year for 16 years.	Collect 100-250 mL of water in a glass or plastic container; analyze immediately.	Field
Conductivity	E120.1/SW9050, direct reading meter	Protocol/Handbook methods.	General water quality parameter used as a marker to verify that site samples are obtained from the same groundwater system.	Every year for 10 years, and every other year for 16 years.	Collect 100-250 mL of water in a glass or plastic container.	Field
Nitrate (NO ₃ ⁻)	IC method E300 or method SW9056; colorimetric, method E353.2	Method E300 is a Handbook method; method SW9056 is an equivalent procedure.	Substrate for microbial respiration if oxygen is depleted.	Every year for 10 years, and every other year for 16 years.	Collect up to 40 mL of water in a glass or plastic container; cool to 4°C; analyze within 48 hours.	Fixed-base

TABLE 7.1 (Continued)
LONG-TERM GROUNDWATER MONITORING ANALYTICAL PROTOCOL
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Analyte	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Sulfate (SO_4^{2-})	IC method E300 or method SW9056 or Hach Sulfa Ver 4 method	Method E300 is a Handbook method; method SW9056 is an equivalent procedure. Hach method is Photometric.	Substrate for anaerobic microbial respiration.	Every year for 10 years, and every other year for 16 years.	Collect up to 40 mL of water in a glass or plastic container; cool to 4°C.	Fixed-base or field (for Hach method)
Redox potential	A2580 B	Measurements are made with electrodes; results are displayed on a meter; samples should be protected from exposure to atmospheric oxygen.	The redox potential of groundwater influences and is influenced by biologically mediated reactions; the redox potential of groundwater may range from more than 200 mV to less than -400 mV.	Every year for 10 years, and every other year for 16 years.	Collect 100-250 mL of water in a glass container, filling container from bottom; analyze immediately.	Field
Methane, ethane, ethene	RSKSOP-114 modified to analyze water samples for methane by headspace sampling with dual thermal conductivity and flame ionization detection.	Method published and used by the USEPA National Risk Management Research Laboratory.	The presence of methane suggests BTEX degradation via an anaerobic pathway utilizing carbon dioxide (carbonate) as the electron acceptor (methanogenesis).	Every year for 10 years, and every other year for 16 years.	Collect water samples in 40 mL volatile organic analysis (VOA) vials with butyl gray/Teflon-lined caps (zero headspace); cool to 4°C.	Fixed-base
Aromatic and halogenated VOCs	Purge and trap GC method SW8021 or GC/MS method SW8260.	If SW8260 is used, a 25-ml purge should be used to lower detection limits.	BTEX are the primary target analytes for monitoring natural attenuation; BTEX concentrations must also be measured for regulatory compliance. Chlorinated solvent concentrations must be measured for regulatory compliance.	Every year for 10 years, and every other year for 16 years.	Collect water samples in a 40 mL VOA vial with zero headspace; cool to 4°C; add hydrochloric acid to pH ≤ 2 .	Fixed-base

a/ Handbook methods are presented by Wiedencier *et al.* (1995b).

TABLE 7.2
POINT-OF-COMPLIANCE GROUNDWATER MONITORING ANALYTICAL PROTOCOL
SITE OT 24
INTRINSIC REMEDIATION TS
MACDILL AIR FORCE BASE, FLORIDA

Analyte	Method/Reference	Comments	Data Use	Recommended Frequency of Analysis	Sample Volume, Sample Container, Sample Preservation	Field or Fixed-Base Laboratory
Temperature	E170.1	Field only.	Well development and purging.	Every year for 10 years, and every other year for 15 years.	N/A	Field
Dissolved Oxygen	Dissolved oxygen meter	Refer to method A4500 for a comparable laboratory procedure.	The oxygen concentration is a data input to the Bioplume model; concentrations less than 1 mg/L generally indicate an anaerobic pathway.	Every year for 10 years, and every other year for 15 years.	Collect 300 mL of water in biochemical oxygen demand bottles; analyze immediately; alternately, measure dissolved oxygen <i>in situ</i> .	Field
pH	E150.1/SW9040, direct reading meter	Protocol/Handbook methods ^a .	Aerobic and anaerobic processes are pH-sensitive.	Every year for 10 years, and every other year for 15 years.	Collect 100–250 mL of water in a glass or plastic container; analyze immediately.	Field
Conductivity	E120.1/SW9050, direct reading meter	Protocol/Handbook methods.	General water quality parameter used as a marker to verify that site samples are obtained from the same groundwater system.	Every year for 10 years, and every other year for 15 years.	Collect 100–250 mL of water in a glass or plastic container.	Field
Redox potential	A2580 B	Measurements are made with electrodes; results are displayed on a meter; samples should be protected from exposure to atmospheric oxygen.	The redox potential of groundwater influences and is influenced by biologically mediated reactions; the redox potential of groundwater may range from more than 200 mV to less than -400 mV.	Every year for 10 years, and every other year for 15 years.	Collect 100–250 mL of water in a glass container, filling container from bottom; analyze immediately.	Field
Aromatic and halogenated VOCs	Purge and trap GC method SW8021 or GC/MS method SW8260.	If SW8260 is used, a 25-ml purge should be used to lower detection limits.	BTEX are the primary target analytes for monitoring natural attenuation; BTEX concentrations must also be measured for regulatory compliance. Chlorinated solvent concentrations must be measured for regulatory compliance.	Every year for 10 years, and every other year for 16 years.	Collect water samples in a 40 mL VOA vial with zero headspace; cool to 4°C; add hydrochloric acid to pH ≤ 2 .	Fixed-base

^a Handbook methods are presented by Wiedemeier *et al.* (1995b).

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SECTION 8

CONCLUSIONS AND RECOMMENDATIONS

This report presents the results of a TS conducted to evaluate the use of intrinsic remediation for remediation of fuel-hydrocarbon-contaminated groundwater in the vicinity of Site OT 24 at MacDill AFB, Florida. Specifically, the finite-difference groundwater model Bioplume II was used in conjunction with site-specific geologic, hydrologic, and laboratory analytical data to simulate the migration and biodegradation of fuel hydrocarbon compounds dissolved in groundwater. To collect the data necessary for the intrinsic remediation demonstration, Parsons ES researchers collected soil and groundwater samples from the site. Physical and chemical data collected under this program were supplemented (where necessary) with data collected during previous site characterization events.

Comparison of BTEX, electron acceptor, and biodegradation byproduct isopleth maps for Site OT 24 provides strong qualitative evidence of biodegradation of BTEX compounds. Geochemical data strongly suggest that biodegradation of fuel hydrocarbons is occurring at the site primarily via the anaerobic processes of sulfate reduction and methanogenesis.

Site-specific geologic, hydrologic, and laboratory analytical data were used in the Bioplume II numerical groundwater model to simulate the effects of advection, dispersion, sorption, and biodegradation on the fate and transport of the dissolved BTEX plume. Extensive site-specific data were used for model calibration and implementation. Model parameters that could not be obtained from existing site data were estimated using common literature values for aquifer materials similar to those found at the site. Conservative input parameters were used to construct the Bioplume II model for this study, and therefore, the model results presented herein are conservative (i.e., the plume should not migrate further than predicted by the models).

For one simulation (model OT 24A), it was assumed that BTEX dissolution from mobile and residual LNAPL in the source area into groundwater would naturally decrease at a geometric rate of 20 percent per year (each concentration was decreased by a factor equal to 20 percent of the previous year's concentration). The results of this model suggest that the plume would not migrate further than 550 feet from the EMTL, and that dissolved BTEX concentrations would decrease below 50 µg/L during simulation year 21 (calendar year 2016). The model predicts that the plume would be completely degraded by simulation year 27 (calendar year 2022).

Model OT 24B assumes that complete source removal via application of an engineered remedial technology such as bioventing and/or biosparging would significantly reduce BTEX dissolution from mobile and residual LNAPL after 4 years.

This assumption is consistent with bioventing results at similar sites (e.g., Patrick AFB, Florida). Results of this model suggest that the source remediation would result in a more rapid decrease in maximum dissolved BTEX concentrations within the plume, causing maximum BTEX concentrations to decrease to below 50 µg/L during simulation year 17 (calendar year 2007). With this scenario, the plume completely disappears by simulation year 22.

Model OT 24C is identical to model OT 24B with the addition of 2 years of groundwater extraction in the source area, and a more rapid remediation of residual and mobile LNAPL (3 years as opposed to 4 years in model OT 24B). The results of this model suggest that the addition of groundwater extraction will further decrease (by approximately 4 years) the time required for maximum BTEX concentrations in the plume to decrease to below 50 µg/L. With this scenario, dissolved BTEX concentrations in the source area decrease to below 1,000 µg/L after 2 years of groundwater extraction, and concentrations decrease to below 50 µg/L after approximately 13 years. The model predicts that the plume will completely disappear after simulation year 19.

The results of this study suggest that natural attenuation of BTEX compounds is occurring at Site OT 24 to the extent that the dissolved concentrations of these compounds in groundwater should be reduced to levels below current regulatory guidelines before potential downgradient receptors could be adversely affected (i.e., the potential contaminant migration pathway will not be complete for any of the potential receptors described in Section 6.2). Model results suggest that LTM and institutional controls may be required for as long as 26 years if an engineered remedial action is not implemented to supplement the effects of intrinsic remediation. If an engineered remedial action is implemented in the source area, then the model results suggest that LTM and institutional controls may be required for approximately 18 to 22 years, depending on the remedial actions taken.

The Air Force recommends intrinsic remediation, institutional controls, and LTM (Alternative 1) as the remedial option for BTEX-impacted groundwater at the site. Given the expected future land uses in the site vicinity (i.e., industrial and/or undeveloped forest), the projected additional cost of source removal via bioventing/biosparging with or without groundwater extraction is not justified by the estimated 4- to 8-year reduction in remediation time resulting from the implementation of source removal activities. Excavation activities in the plume area and groundwater use in and downgradient from the plume area should be restricted for an estimated maximum of 26 years. In addition, proper health and safety precautions should be followed in the event that excavation is performed in the contaminated area. A site-specific remedial action plan, including a detailed SAP, should be submitted to the FDEP for approval prior to implementation of the recommended remedial alternative for Site OT 24. The evidence supporting the occurrence of CAH biodegradation in groundwater, and the low magnitude of CAH concentrations detected at the furthest downgradient sampling point, suggest that Alternative 1 is also appropriate for CAHs dissolved in groundwater beneath the site.

Prior to finalization of LTM and POC well locations, and implementation of the LTM plan, groundwater flow and contaminant migration directions should be more completely defined using water level data from all available monitoring well/points,

including wells installed at the adjacent POL tank farm. The downgradient extent of the dissolved BTEX plume should also be more fully defined to ensure that it does not extend to a potential discharge area such as the mangrove swamp, and to facilitate LTM. On the basis of currently available data, it is estimated that this objective could be accomplished by installing four plume-definition wells in the forested area south of monitoring point 24PZ-1, near the estimated downgradient plume boundary. Once it is decided that the groundwater monitoring points installed for this intrinsic remediation demonstration will not be used for future resampling, they should be abandoned according to state requirements.

To verify the results of the Bioplume II modeling effort, and to ensure that natural attenuation of BTEX and CAHs is occurring at rates sufficient to protect potential downgradient receptors, groundwater from five LTM wells should be sampled annually to biannually and analyzed for the parameters listed in Table 7.1. Three of the proposed LTM wells would be installed adjacent to existing monitoring wells/points MD24-2, 24MP-1, and 24PZ-1. A fourth LTM well would be installed approximately 175 feet south of 24PZ-1, and existing well MD24-6 would be the fifth LTM well. In addition, three POC groundwater monitoring wells should be installed downgradient from the predicted maximum travel distance of the BTEX plume (Figure 5.12) and sampled annually for the parameters listed in Table 7.2. Figure 7.1 shows suggested locations for the LTM and POC wells. These wells should be sampled annually until plume stabilization or recession is demonstrated, and then biannually thereafter. If dissolved contaminant concentrations in groundwater in the POC wells exceed state guidelines for no further action of 50 µg/L for benzene and total BTEX or 1 µg/L for vinyl chloride, then additional evaluation or corrective action may be necessary at this site.

SECTION 9

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